

CHAPTER 8

FUELS: PROCESSING, STORAGE, TRANSMISSION, DISTRIBUTION, AND SAFETY

8.1 HYDROGEN: THE IDEAL FUEL

8.1.1. Hydrogen: The Most Electroactive and Environmentally Clean Fuel for All Types of Fuel Cells

Since the invention of the fuel cell by Sir William Grove in 1839, it has been well recognized that hydrogen is the ideal fuel for all types of fuel cells. The major accomplishments in fuel cell R&D during the 19th and 20th centuries, were:

- the proposition by the eminent physical chemist Friedrich Wilhelm Ostwald that the direct conversion of chemical energy to electricity would have a great effect on energy conservation and on minimizing environmental pollution;
- the development of a 5 kW alkaline fuel cell, using hydrogen and oxygen, by Francis T. Bacon, which was started in 1932 and completed in 1952;
- the discovery of the proton-exchange membrane fuel cell (referred to as the solid polymer electrolyte fuel cell, from its birth in the 1960s) and its use in NASA's Gemini space flights as an auxiliary power plant in the 1960s; and
- following Bacon's discovery, the development of highly efficient hydrogen/oxygen advanced alkaline fuel cells initially by Pratt and

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Whitney and subsequently by International Fuel Cells (Division of United Technology Corporation) and their applications as an auxiliary power source for NASA's Apollo and space shuttle flights from the late 1960s until the present time.

The Chapters on Basic Electrochemistry (Chapters 1 to 3) and the Fundamental Aspects of Fuel Cells (Chapters 4 and 5) clearly demonstrate the reasons for pure hydrogen being the preferred fuel for all types of fuel cells. The most important reason is that it is the most electroactive fuel in a fuel cell i.e., it has exchange current densities for the anodic reaction that are at least three to five orders of magnitude higher than that of any other fuel at low to intermediate temperatures. In the molten-carbonate and solid-oxide fuel cells, carbon monoxide, a product of the steam-reforming reaction, is also quite electro-active. However, here too one could interpret that the anodic reaction occurs via hydrogen because on the anode electrocatalyst, the shift conversion reaction could produce hydrogen. Methanol is reasonably active in low temperature fuel cells and perhaps, in the future, this fuel and ethanol may have some prospects for direct use in MCFCs and SOFCs. The hydrocarbon fuels are considerably less active than alcohols. Further, the use of pure hydrogen might facilitate the design of fuel cell systems. In fuel cell vehicles, for example, the vehicle is likely to be less complex, more energy efficient, have better performance, and cost less if hydrogen is used directly on board.

There are other potential societal benefits of using hydrogen as a future energy carrier. Roughly two thirds of current global greenhouse gas emissions are associated with direct combustion of fuels for transportation and heating (the remainder of emissions come from electric power generation). There is a rising international concern about the potential effects of global climate change, associated with emissions of CO₂ from fossil fuel use, and increasing levels of CO₂ in the atmosphere. Many countries have signed the Kyoto conference agreement to reduce the level of CO₂ emissions by 10%, from 1990 levels, by the year 2010, and there are continuing efforts by various countries to limit CO₂ emissions. In addition, a significant fraction of air pollutant emissions and about two thirds of primary fossil energy use are associated with the direct use of fuels. A variety of alternative transportation fuels and of efficient, low-polluting vehicle technologies have been proposed to help address these challenges. Of these, hydrogen, used in fuel cells, offers the greatest potential for simultaneously reducing emissions of greenhouse gases and air pollutants.

Hydrogen, like electricity, is an *energy currency* or an *energy carrier* that must be produced from other primary resources such as fossil fuels, renewables, or nuclear power. Hydrogen can be made from a variety of primary resources including fossil fuels (natural gas or coal), renewables (biomass, hydropower, wind, and solar), and nuclear power. If hydrogen is made from renewable energy sources or from fossil fuels with capture and sequestration of CO₂, it would be possible to produce and use energy with near zero emissions of greenhouse gases or air

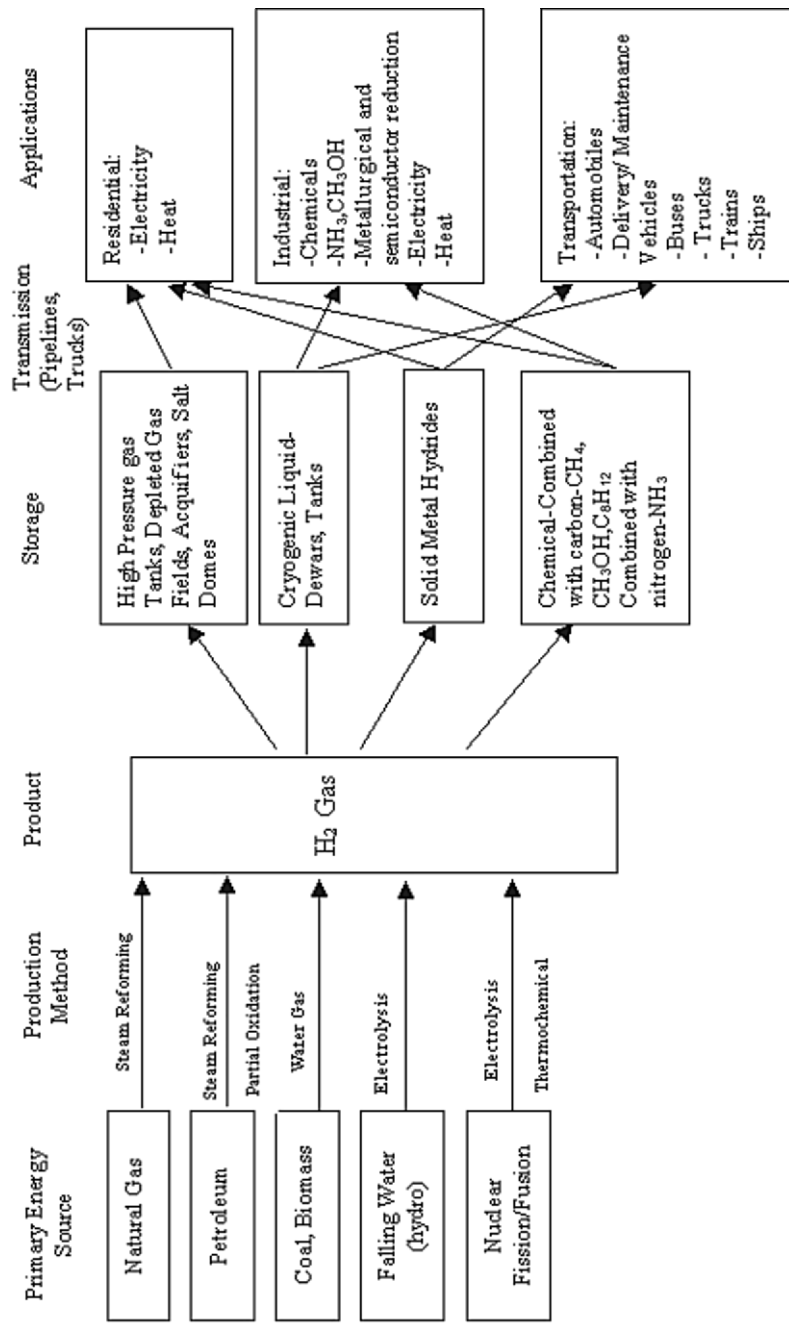


Figure 8.1. Modus operandi of a hydrogen-energy scenario.

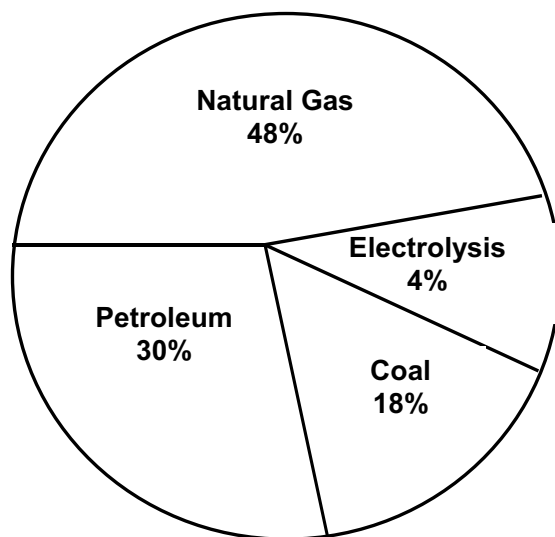


Figure 8.2. Global production sources of hydrogen.

pollutants. The following Section describes possible scenarios for a *hydrogen-energy system*.

8.1.2. A Modus Operandi for a Hydrogen Energy Scenario

In a review article published about 18 years ago,¹ a clear illustration was presented to demonstrate the modus operandi of a hydrogen-energy system (Figure 8.1), which takes into consideration that hydrogen is an energy currency/energy carrier. First, the hydrogen has to be produced from a primary energy source. Second, one must consider the most efficient and economic method for its production. Third, hydrogen is produced in a gaseous state. The method of its storage will depend on the application and the economy of scale. Fourth, the hydrogen will have to be transmitted to the site of application. Fifth, there is a multitude of applications. In Figure 8.1, these are classified under residential, industrial, and transportation applications.

Hydrogen is produced on a large scale today for chemical applications such as ammonia and methanol synthesis and oil refining. The total world hydrogen production is about 500 billion Nm³ per year. This is equivalent to about 2% of the world's primary energy consumption. Globally, about 48% of hydrogen is made from natural gas, about 30% from oil, 18% from coal, and 4% from water

electrolysis (Figure 8.2). Of this amount, about 50% is used in ammonia production

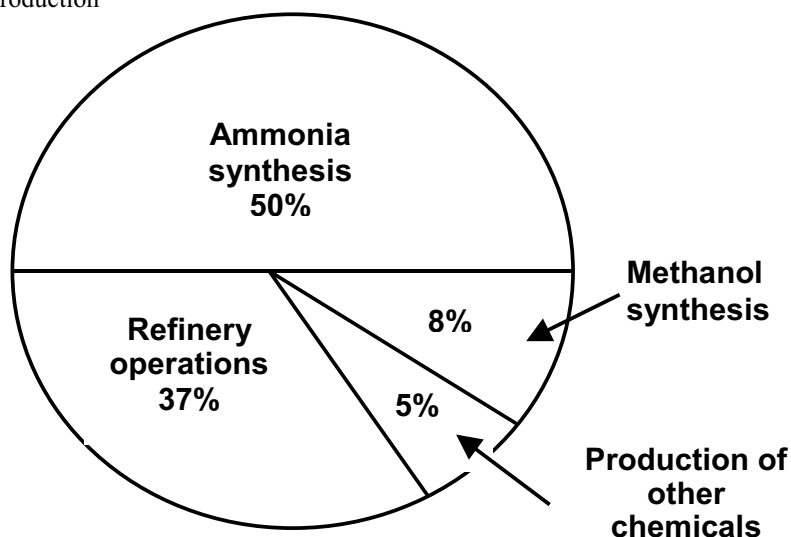


Figure 8.3. Global consumption of hydrogen.

for fertilizer, 37% for petroleum refining, 8% for methanol synthesis, 4% for other chemical uses, and 1% for aerospace (Figure 8.3). About 90 billion Nm³ per year are produced in the US today, primarily for chemical and refining applications.² This is equivalent to about 1% of the US primary energy use. In the United States, about 95% of the hydrogen is currently produced from steam-reforming of natural gas, and the remainder via recovery as by-product from chemical operations (such as chlor-alkali plants), partial oxidation of hydrocarbons (such as coal or petroleum residuals at refineries), or by electrolysis of water. If in the future hydrogen is widely used as an energy carrier, its production would increase greatly beyond the current industrial levels.

Historically, there has been a trend toward *decarbonization* of the energy system. This was shown in studies carried out by Marchetti et al.,³ and Nakicenovic et al.⁴ It was shown that there is a semi-logarithmic relation for the hydrogen to carbon (H/C) ratio in the world's fuel mix as a function of time (Figure 8.4). The relationship is striking, and we are presently in an era where the H/C ratio is 4, as evidenced by the relatively high utilization of natural gas as a fuel. This decarbonization of the energy supply would have to continue at several times the historical rate to assure that atmospheric concentrations of CO₂ remain at levels that are twice the pre-industrial level or less. As noted above, presently fuels contribute

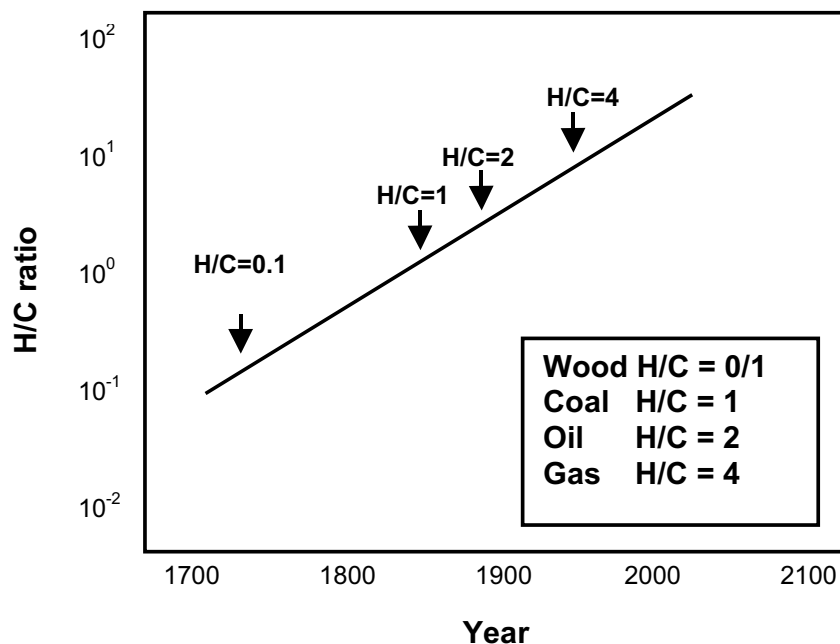


Figure 8.4. Global evolution of H/C ratio in the world's fuel mix.

to over half of the global greenhouse-gas emissions. Even if the electricity production sector is completely decarbonized, emissions from the fuel sector will have to be decreased by a factor of 3 to 5 by the end of the 21st century to achieve stable levels of atmospheric CO₂, i.e., 450-550 ppm.

The methods for production of hydrogen from the primary energy and renewable energy sources are dealt with in Sections 8.1.3 to 8.3.6. Section 8.4 summarizes methods of production of other fuels for direct or indirect utilization in fuel cells. Fuel storage, transmission, distribution, and safety are discussed in Sections 8.5 to 8.7.

8.1.3. Fossil Fuels: The Main Source of Hydrogen for the Foreseeable Future

Figure 8.2 clearly illustrates that the fossil fuels, natural gas, petroleum, and coal are the primary energy sources contributing to the production of more than 95% of hydrogen for the chemical and petroleum refining industry today. In recent years, there has been a trend by the petroleum industry to produce hydrogen from natural gas rather than from residual fuel oil for the hydrocracking of the heavier

fractions of petroleum; the purpose was to enrich the production of gasoline and diesel fuel. The main reason for the use of natural gas to produce hydrogen is that fuel processing with natural gas is cleaner and more economical. In some countries (China, India, Germany, and South Africa), the extent of utilization of coal as a primary energy source for the production of hydrogen is higher than in the USA. Another interesting fact is that during World War II, the Germans and the Japanese developed the technology for production of coal-derived gasoline, using hydrogen that was also produced from coal. In view of the relative abundance of natural gas and coal, these primary energy sources will continue to contribute significantly to the production of hydrogen, even in the era of a *hydrogen energy scenario*, in which the demands for hydrogen could increase many times over that for hydrogen required by the chemical industry.

Pure hydrogen can be produced from fossil fuels for storage and subsequent use in a fuel cell, or a hydrogen rich gas can be produced in a fuel processor, integrated with a fuel cell. Methods for pure hydrogen production from natural gas and coal are described in Sections 8.1.4 to 8.1.6. The topic of fuel processors for hydrogen production for integration with fuel cells will be dealt with in some detail in Section 8.2. Methods of hydrogen production from renewable and nuclear sources are addressed in Section 8.3.

8.1.4. Natural Gas: The Most Promising Fuel for All Types of Fuel Cells

Since the 1990s, a stronger emphasis has been made on the utilization of natural gas as a primary energy source for all types of fuel cells.⁵ This approach was further reinforced by the increased attraction for its use in fuel cell/gas turbine hybrid systems. Further, since natural gas is a considerably cleaner fuel for fuel processors than petroleum or coal and the hydrogen content is higher for the former than for the latter two fuels, the main goals of the major worldwide fuel cell programs are to use natural gas or natural-gas derived fuels. Figure 8.5 provides a vision of such an approach for all types of fuel cells. This figure also illustrates the applications of these types of fuel cells. For the low temperature, acid (PEMFC) and alkaline electrolyte (AFC) fuel cells, pure hydrogen is the desired fuel. The fuel processing involves steam reforming, shift conversion, preferential oxidation, and pressure swing absorption (see Section 8.2.1). Natural gas is also abundantly used for the production of methanol. Methanol, a liquid fuel, which has values of specific energy and energy density equal to about half those for gasoline, is an ideal fuel to be carried on board for transportation vehicles. The production of methanol from natural gas involves the combination of products of the steam-reformer reaction (H_2 and CO). The methanol can be used directly in a PEMFC or subjected to further fuel processing to produce hydrogen, as shown in Figure 8.5. The PAFC and PEMFC will be the most appropriate fuel cells for use of methanol or hydrogen produced by this route and the applications are multifold: power generation, electric vehicles, stand-by power, and remote power. An advantage of the PAFC is that its operating

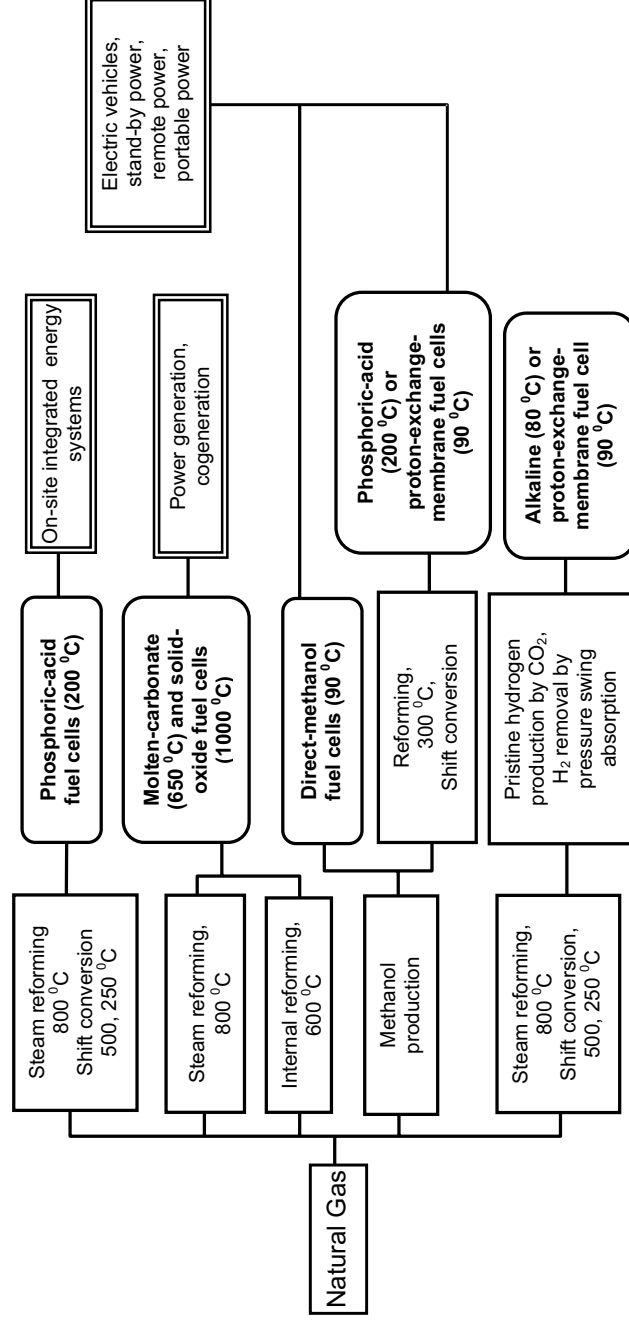


Figure 8.5. Natural gas: the ideal fuel for all types of fuel cells. Demonstrated and potential applications of fuel cells are marked on bold. Reprinted from Reference 5, Copyright (2001) with permission from Plenum Press.

temperature is about 200 °C, and at this temperature, a 1 to 2% level of CO in the H₂ produced by steam-reforming/shift-conversion of natural gas is not a poison. Thus, the step of preferential oxidation is not required. The PAFC technology is well established with this fuel-producing technology, and PAFC systems ranging in power level from 40 kW to 10 MW have been demonstrated. The major advance has been with UTC-fuel cells commercializing the 200 kW natural gas fuelled power plant (the PC-25) for cogeneration applications. The advantages of the high temperature MCFC and SOFC systems are that the steam-reforming shift conversion in the electrochemical stack is more than adequate for the anodic oxidation of not only hydrogen, but also of carbon monoxide. Such types of direct fuel cells are being developed for power generation and cogeneration applications (see Chapter 9 for details).

8.1.5. Coal Gasifiers for Hydrogen Production

Due to the relative abundance of coal in several countries in the world (an estimate is that it can satisfy the energy requirements of mankind for the next 500 years), there has been enthusiasm during the past 50 years for using gasified coal products in fuel cells. Basically, there are three types of coal gasifiers: moving beds, fluidized beds, and entrained beds. Steam, oxygen, or air is used to partially oxidize the coal. The moving bed gasifier mainly produces gaseous hydrocarbons, methane and ethane, and liquid fuels such as naphthalene, tars, oils, and phenolics at a temperature in the range 425 to 650 °C. The entrained bed gasifier operates at a high temperature (above 1250 °C) and the products are mainly H₂, CO, and CO₂. The fluidized bed gasifier has an intermediate temperature for operation (925 to 1040 °C), and the products are composed of a mixture of gases, as generated in other types of gasifiers. The heat needed for the reactions, in all three cases, is supplied by the exothermic reaction, i.e., the partial oxidation of coal. Impurities include H₂S, COS, NH₃, HCN, particulates, tars, oils, and phenols. These are removed by hot gas or cold gas clean-up technologies. The latter methods consist of uses of cyclones and particulate scrubbers, COS hydrolysis reactors, liquid scrubbers for NH₃ and H₂S, and sulfur recovery (Claus process). All these requirements make the systems complex and expensive, and there is also the need for heat exchangers and coolers. For the various types of oxygen-blown gasifiers the yield of hydrogen varies from about 15 to 30% and that of CO from 5 to 60%. However, if relatively pure hydrogen is the desired product, a shift converter, an acid-gas removal system, and a methanator could be incorporated with the coal gasifier system, as used in the Koppers-Totzek atmospheric pressure and the pressurized Texaco and Shell processes. The hydrogen content from these gasifiers is about 95%.

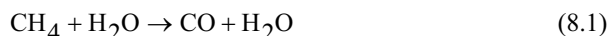
8.2 FUEL PROCESSORS FOR INTEGRATION WITH FUEL CELLS

8.2.1. Steam-Reforming, Shift-Conversion, Pressure Swing, and Adsorption of Natural Gas for Ultra-Pure H₂ Production for AFCs and PEMFCs

The ideal fuel for a PEMFC or an AFC is ultra pure hydrogen. When natural gas is used as the primary fuel for pure hydrogen production, several chemical steps are performed: sulfur removal, steam-reforming, shift-conversion, and hydrogen purification (via pressure swing adsorption).

It is essential to first remove the sulfur from natural gas by passing the feed-stream at 290-370 °C over a Co-Mo catalyst in the presence of 5% H₂ in order to remove the sulfur as H₂S. The out-flowing gas is then cooled and scrubbed with a mono-ethanol amine solution, followed by its absorption over a ZnO catalyst at 340 to 370 °C to reduce the sulfur content to about 0.5 ppm.

The next step is to pass this gas through the steam-reformer where the following reactions take place:



The first reaction (methane plus steam-reforming reaction) is endothermic, while the second (water gas shift-reaction) is exothermic. It must be noted that the water gas shift-conversion reaction does not take place completely. The catalyst for the reformer reaction is nickel oxide supported on calcium aluminate, alumina, or calcium aluminum titanate. The operating temperature is 650 to 700 °C and the pressure is between 22 and 24 atm. The outlet gas temperature is 870-885 °C. The product composition is 76% H₂, 12% CO, 10% CO₂, and 1.3% CH₄.

The subsequent step is to further carry out the water gas-conversion shift reaction for a nearly complete conversion of the CO to CO₂. This is done in two stages: (i) in a high temperature shift reactor at 340-350 °C using chromium promoted iron oxide catalyst; and (ii) in a low temperature shift reactor at 200-300 °C over a Cu-Zn catalyst, supported on alumina catalyst. The output mixture of gases is cooled by a regenerative scrubbing process to produce 98% H₂, 0.3% CO, 0.019% CO₂, and 1.5% CH₄. The residual gases are converted to CH₄ (methanation reaction) by passing the gases reheated to 315 °C over a nickel oxide catalyst. These intermediate steps are schematically illustrated in Figure 8.6. The hydrogen can be further purified by a cryogenic procedure.

If there is a need for ultra pure hydrogen, the use of the pressure swing absorption (PSA) method for hydrogen purification is attractive. The process diagrams for conventional scrubbing and pressure swing absorption are represented

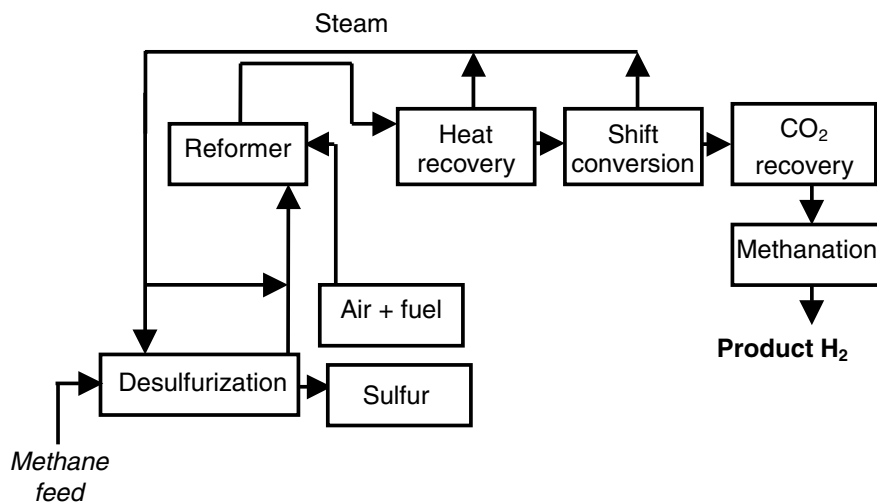


Figure 8.6. Flowchart for ultra-pure hydrogen production by conventional steam-methane-reforming/shift-conversion of natural gas.

in Figure 8.7. The advantage of the PSA method is that it eliminates the low temperature shift, CO₂ scrubbing, methanation, and cryogenic steps. The PSA method involves passing the product gases from the high temperature shift reactor into an absorbent bed, which removes all the constituents except H₂. To regenerate or reactivate the bed, the reactor is depressurized, purged with hydrogen, and repressurized. During this process, the feed is switched to another bed that is in parallel with the bed being reactivated. The main advantages of the PSA method are:

- lower maintenance costs,
- higher reliability,
- efficient heat recovery, and
- higher efficiency than a conventional plant, 84.6% vs. 83.2%, respectively.

The hydrogen produced by the conventional and PSA methods is therefore ideally suited for use in PEMFCs and AFCs.

8.2.2. Steam Reforming, Shift Conversion, and Preferential Oxidation of Natural Gas, Gasoline or Methanol for PEMFCs

The PEMFC has an acid electrolyte environment. Thus, unlike in the case of an AFC, it is not necessary to remove CO₂ from the product gas stream after the steam-reforming and water-gas shift reactions. However, since the product gas may contain

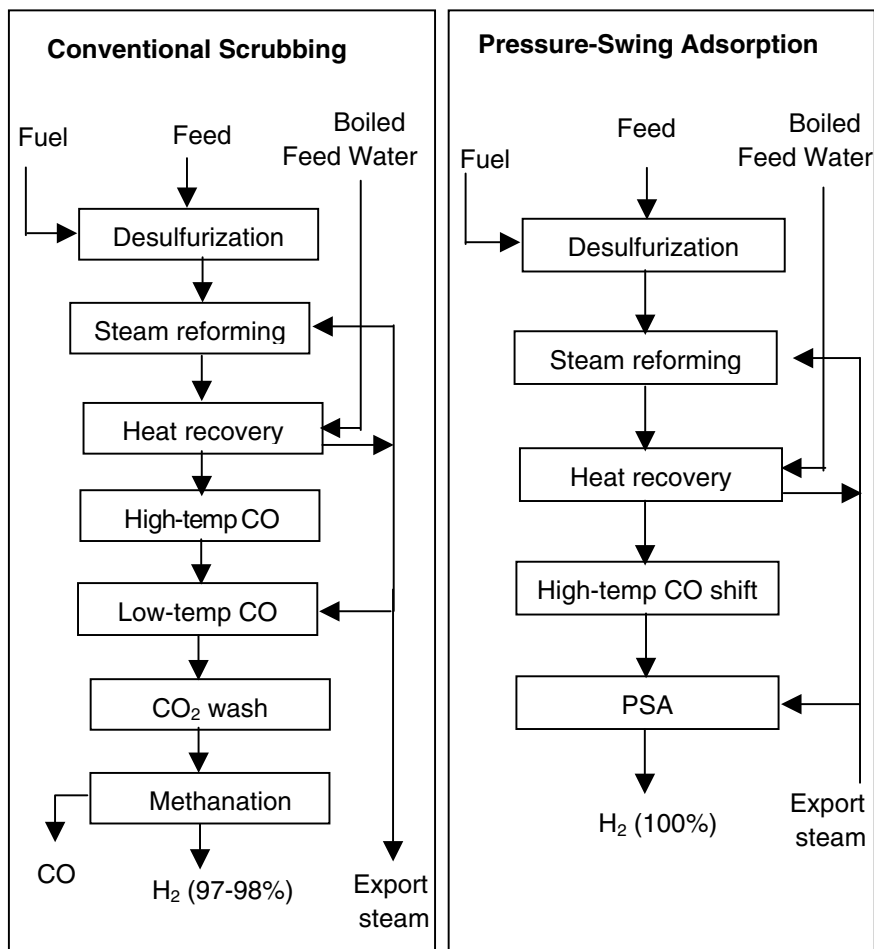


Figure 8.7. Flow charts for production of ultra-pure hydrogen using the conventional scrubbing and pressure swing absorption (PSA) methods.

0.5-1.0% of CO—a deadly poison for the anode in the PEMFC—an additional fuel-processing step is necessary, i.e., the preferential oxidation of this gas in a separate chamber after the low-temperature shift reactor (Figure 8.8). The exit gases from this reactor are passed through a platinum-on-alumina catalyst into the preferential

oxidizer reactor along with 2% air. The CO is first selectively adsorbed on this catalyst and then oxidized by the air to CO₂. Until recently, the quoted value for the

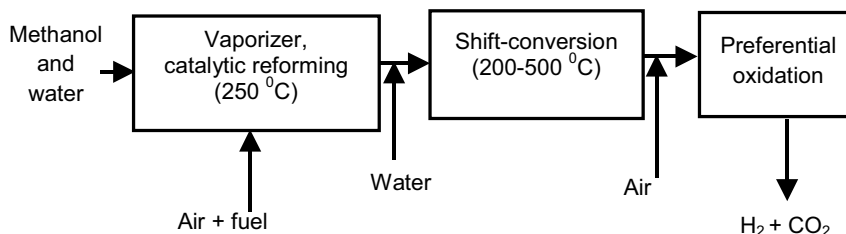


Figure 8.8. Typical steam-reforming/shift-conversion/preferential-oxidation of natural gas, gasoline, or methanol for PEMFCs. The flow chart shown is for hydrogen production from methanol.

reduction in CO level was 500 ppm, when hydrocarbons were used as fuels and 50 ppm when methanol was used as the fuel. However, more recently Epyx Corporation (now Nuvera Fuel Cells) claimed that they could reduce the CO level to 10 ppm when gasoline was the fuel to be processed.⁶ The PEMFC can tolerate this level of CO at 80 °C without any substantial anode poisoning.

There has been great interest in the use of this type of fuel processor to be carried on board a PEMFC-powered-transportation vehicle. The advantage of methanol is that it is a partially oxidized fuel (as compared with hydrocarbons) and the first step of its steam-reforming requires a considerably lower temperature (280 to 300 °C) than that for hydrocarbons. Further, the product gas from the entire fuel processing has less than 50 ppm CO, whereas the CO levels are higher with hydrocarbons. However, there has been more emphasis on gasoline fuel processing by the US Department of Energy. The reason for this is the large availability of petroleum resources (gasoline) for at least the next 20 to 30 years as well as the higher energy density for gasoline as compared to methanol (about twice, on both, weight and volumetric bases).

Methanol is produced from the primary fuel—i.e., natural gas—on a large scale by the plastics industry for the production of formaldehyde. The products of the steam-reforming reaction (Eq. 8.1) are passed through a reactor using a CuO-ZnO catalyst for the formation of methanol:



Coal is another abundant primary energy source for methanol production. In this case, the products of the coal-gasification reaction, i.e.,



are combined in the same manner, as expressed by Eq. (8.3), to form methanol. In developing countries, there is also interest in methanol production from biomass (see Section 8.3.5).

8.2.3. Steam-Reforming and Shift-Conversion of Natural Gas or Methanol for H_2 Production for PAFCs

An attractive feature of the PAFC is that it operates at a temperature of about 200 °C and at this temperature the tolerance level of CO by the anode Pt electrocatalyst is about 1%. Thus, the heavy and bulky preferential oxidation reactor is not required. Further, the waste heat from the PAFC is of reasonably high quality, and it can be used for the production of steam required for the reformer reaction.

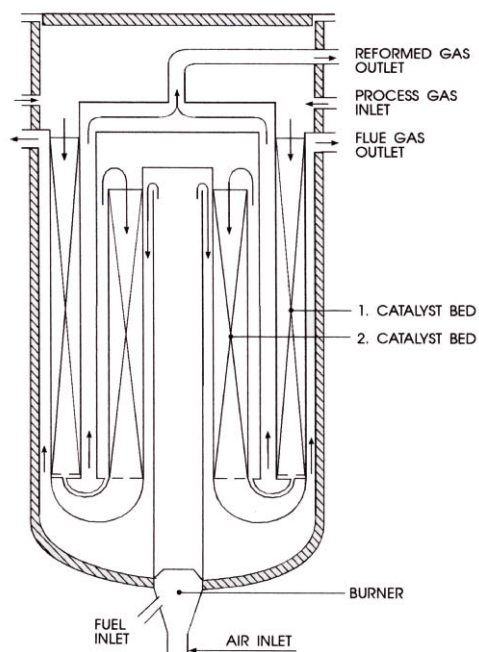


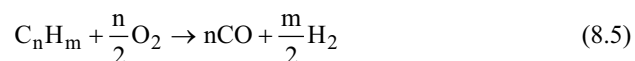
Figure 8.9. Design of a UTC fuel-cell regenerative-tube reformer for hydrogen production from natural gas and use in PAFCs. Reprinted from K. Kordesch and G. Simader, *Fuel Cells and their Applications*, VCH, Weinheim, Copyright (1996), with permission from Wiley, VCH.

The heat utilization is even more effective when methanol rather than natural gas is used as the fuel because the reformer reaction, required for the former is about 300 °C, while for the latter it is about 650–700 °C.

There are three types of reforming furnaces, used for hydrogen production: (i) a top fired with co-current flow of the process and synthesis gases; (ii) a bottom fired with counter-current flow of gases; and (iii) a side-fired reactor with a homogenous heat flux along the entire length of the tube. UTC Fuel Cells, the leading PAFC developer in the world, uses a regenerative-tube reformer.⁷ The design of this reformer uses a combination of counter-current and co-current flows of the reactant gases and effluents (Figure 8.9). In this design, the radiant heat transfer occurs from the flu gas to the catalyst-filled annulus on one side, and heat transfer to the other side takes place via the process gas. The reactor is compact and the heat savings are significant. It was originally designed by Haldor Topsoe and was further developed by UTC Fuel Cells for fuel cell applications.

8.2.4. Partial Oxidation and Shift Conversion of Hydrocarbons and Alcohols for PEMFCs

Hydrogen and hydrogen-rich synthesis gas can be produced by non-catalytic partial oxidation of hydrocarbons (e.g., refinery, residual oil) using the Texaco or Shell processes. The overall reaction is:



The process diagram for the complete conversion to hydrogen, with acid gas removal and with sulphur separation is shown in Fig. 8.10. Partial oxidation of the hydrocarbon occurs with less than the stoichiometric amount of oxygen at 1300 to 1400 °C. The high temperature and low temperature shift reactions are then carried out. The heat recovered from the shift reaction is utilized for steam production. The hydrogen produced from this process is approximately 97.5% pure (i.e., after CO₂ removal, as in the steam-reforming-shift-conversion process).

EPYX Corporation, Nuvera, and IFC have been actively engaged in the development of fuel flexible fuel processors of this type to be integrated with 50 kW PEMFC fuel cell stacks from IFC and Plug Power in the PNGV program. The fuels include gasoline and methanol. One of the problems encountered with this type of fuel cell processor for automotive applications is that the intermediate steps of shift conversion, preferential oxidation, and air bleeding are necessary. As a consequence, the start-up time from ambient temperature is about 5 to 10 minutes. There is also a significant energy penalty, and the CO content is enhanced during transients.

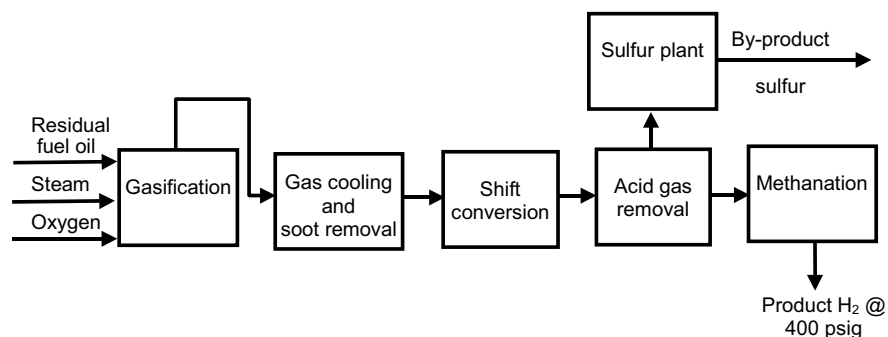
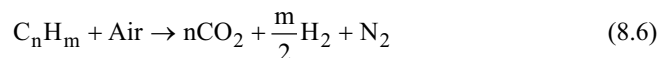


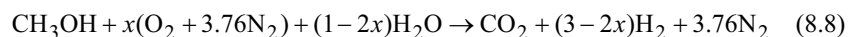
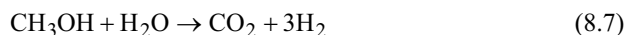
Figure 8.10. Flowchart for ultra-pure hydrogen production from hydrocarbons by partial-oxidation→shift-conversion→ acid-gas-removal→methanation.

8.2.5. Autothermal Reforming of Methanol and Gasoline for PEMFC Powered Vehicles

This novel method is being developed at Argonne National Laboratory (ANL).⁸ Basically, three methods of fuel processing have been considered and/or developed for on-board fuel processing in PEMFC powered vehicles: steam reforming, partial-oxidation reforming, and autothermal reforming. The steam-reforming fuel processor has the disadvantage of reactor design with inefficient heat transfer from the shift-reactor to the steam-reformer. Thus, it is not effective enough for rapid start-up and transient response in automobiles. Partial oxidation fuel processing involves a very high temperature (over 1000 °C) for the first step, which is exothermic:



By injecting an appropriate amount of steam into the system, the steam reforming reaction can be carried out. The partial oxidation step can occur with or without a catalyst. The auto-thermal reforming process is a hybrid of the steam-reforming and partial oxidation fuel processors. When methanol is used as the fuel, the autothermal reforming process is represented by:



in which x is less than 2.3%. This type of fuel processor is being developed by Johnson Matthey and by Argonne National Laboratory. By carrying out the reactions in the presence of catalysts, the operating temperature can be lowered, thus favoring the water-gas shift reaction. The lower temperature also favors reduction in fuel consumption. To inhibit coke formation, the oxygen/carbon ratio in the inlet stream to the reactor is optimized. Steam is used as a source of oxygen to lower the temperature, which is necessary to avoid coke formation. Autothermal reformers are also designed for efficient heat transfer from the exothermic partial oxidation intermediate step to the steam-reforming of the fuel in the same reactor. A laboratory scale design of the reactor used by Argonne National Laboratory is shown in Figure 8.11. The fuel, water, and air are introduced via a nozzle into the reactor containing a zinc oxide/copper oxide catalyst. A small electric coil is used to ignite the mixture. The product gases exit at the bottom and are periodically analyzed by an on-line gas chromatograph. Catalyst materials are also evaluated in the packed bed micro-reactor (Figure. 8.11). The temperature is controlled using a surrounding furnace. Using methanol as the fuel at a feed rate of 54 ml/min, 35-50 ml/min of air, and 10-20 ml of water, the products are 50% H_2 , 20% CO_2 , and 1%

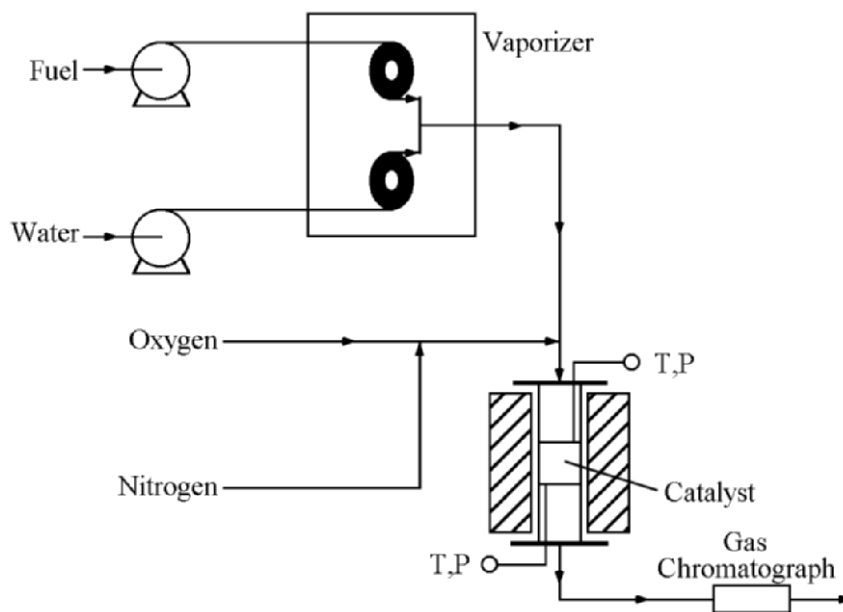


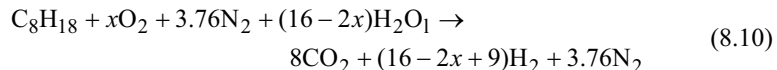
Figure 8.11. Laboratory-scale design of an autothermal reformer for hydrogen production from methanol or gasoline, evaluation of catalyst materials, and on-line chromatography product analysis by Argonne National Laboratory. Reprinted from Reference 9, Copyright (1997) with permission from the authors.

CO. It must be noted that it is assumed in Eq. (8.7) that air and oxygen are both used for the partial oxidation intermediate step. The parameter, x , is the oxygen to methanol molar ratio ($0 < x < 0.5$). The enthalpy change for the reaction, ΔH , is given by:

$$\Delta H = 131.572 \text{ kJ/mol CH}_3\text{OH} \quad (8.9)$$

This assumes that all species are in their standard states at 25 °C. The reaction is thermoneutral at $x = 0.23$.

The conversion of gasoline (e.g., octane) to H_2 may be expressed by:



where x is the oxygen/fuel molar ratio ($0 < x < 4$). The enthalpy change for the reaction is:

$$\Delta H = 1685.572 \text{ kJ/mol C}_8\text{H}_{18} \quad (8.11)$$

The reaction is thermoneutral at $x = 2.94$. With a proprietary catalyst used by ANL, the hydrogen content in the exit gas of the reactor was over 50%. With O_2 instead of air for the partial oxidation step, the hydrogen content could be increased to over 60%.

Figure 8.12 shows a comparative performance analysis of the three pathways for hydrogen production from hydrocarbon and alcohol fuels.^{9,10} The steam reformer/shift conversion pathway presents the challenge of separating water from the combustion products and its subsequent feed for the reformer reaction. Because of this, heat is only extracted from the combustion process and the products are vented into the atmosphere. The partial oxidation and autothermal reforming processors are more energy-efficient, compact, and lightweight; these reactions are thus more attractive for on-board fuel processing. Such types of fuel processors produce hydrogen at considerably lower levels than in large industrial-scale hydrogen generation plants using steam-reforming/shift-conversion and coal gasification processes. The former type of fuel processors must meet some stringent requirements:

- frequent cyclability, i.e., start-up and shut down;
- ability to provide hydrogen at transient rates for start-up and acceleration (this may cause problems of enhancing CO levels);
- high rate of manufacturability to achieve low capital cost (equivalent to about \$50/kW); and
- high reliability and lifetime of at least 10 years.

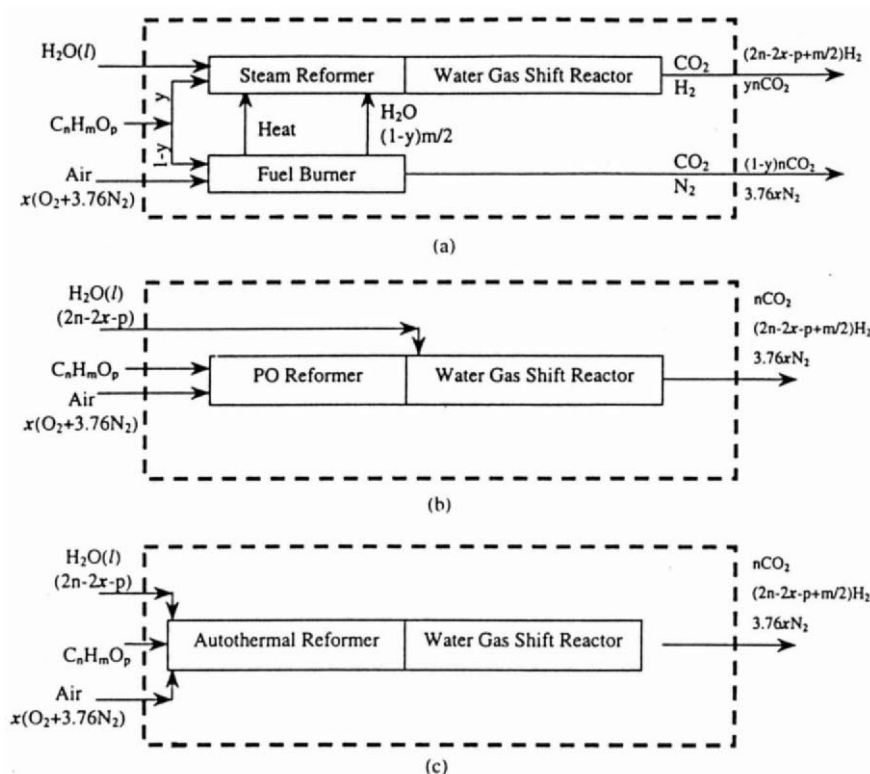


Figure 8.12. Comparative pathways for hydrogen production using hydrocarbon and alcohol fuels. Reprinted from Reference 10, Copyright (2001), with permission from Elsevier.

One other important aspect is that coke formation must be prevented by operating at a high temperature, with high oxygen to carbon atomic ratios. The oxygen is generally fed as water into the fuel processors for this purpose.

Scaled-up versions of such types of fuel processors have been designed, developed, and tested by ANL, EPYX/A.D Little, Nuvera, and UTC-IFC (present name UTC Fuel Cells).⁷ The ANL unit has a H_2 generation capacity of 6 kW and includes the catalytic autothermal reformer, a zinc oxide bed for sulphur removal, and a water gas shift reactor. The catalysts were developed at ANL. This reactor produced hydrogen at a composition of 40% with less than 4% CO. The EPYX/A.D Little fuel processor was built to be integrated with a 50 kW PEMFC and claims were made that the CO level from the shift reactor could be reduced to 10 ppm. The Nuvera unit was also built for coupling with a 50 kW PEMFC from Plug Power; UTC-Fuel Cells developed their own fuel processors for integrating with their 50 kW PEMFC. The Nuvera unit is pressurized; the UTC-Fuel Cells unit operates at

ambient pressure. The projected specific power and power density for integrated fuel processor/fuel cell system are 140 W/kg and 140 W/l; these values were about half those targeted for the year 2004 in the PNGV program.⁶ The start-up time is currently about 10 minutes, while the target in 2004 was considerably less than a minute.

8.2.6. Steam Reforming of Natural Gas for MCFC or SOFC: Gas Turbine Hybrids

Fuel processing is greatly simplified for the high-temperature MCFCs and SOFCs as compared with that for the low and intermediate temperature fuel cells. As illustrated in Figure 8.5, the process only involves the steam-reforming of natural gas to produce H_2 and CO. Carbon monoxide like H_2 , is an anodic fuel in MCFCs and SOFCs and not a poison, as in the low and intermediate temperature PEMFCs and PAFCs. Though it is very possible that the oxidation of the CO occurs electrochemically on the nickel-based electrocatalysts in the MCFCs and SOFCs, it is equally probable that the shift conversion reaction occurs first on this electrocatalyst to produce hydrogen, which is then electro-oxidized.

Fuel processors for these types of fuel cells are of two types:

- the fuel processor sub-system is a unit separated from the electrochemical cell stack; (i.e., the external reformer); and
- the fuel processor is integrated with the electrochemical cell stack (i.e., the internal reformer).¹¹

The latter is the most favored processor and it was developed by Fuel Cell Energy. Its advantage is that the heat required for the endothermic reforming reaction ($\Delta H = 225.18$ kJ/mol) is directly transferred from the heat generated in the exothermic fuel cell reaction in the electrochemical stack. Thus, the need for an auxiliary heat exchanger is eliminated.

The internal reformer may be further divided into two types: the indirect internal reformer (IIR) and the direct internal reformer (DIR) (see Figure 8.13). In the IIR, the reformer catalyst is separated from the fuel cell electrocatalyst, whereas in the DIR the fuel cell electrocatalyst serves also as the reformer catalyst and because of the hydrogen being instantly consumed in the fuel cell, the methane reformation reaction is accelerated. In both these types, the heat transfer is efficient, without a separate heat exchanger and the product steam, formed by the fuel cell reaction, accelerates the reformer and shift conversion reactions to produce more hydrogen. The extent of methane conversion increased with the amount of fuel utilization, i.e., in a DIR MCFC at 650 °C and 1 atm pressure with the steam/carbon ratio being maintained at 2, therefore there was more than 99% of methane conversion when the fuel utilization in the MCFC was greater than 65%. In the IIR, nickel supported on MgO or $LiAlO_2$ was used as the electrocatalyst. Internal

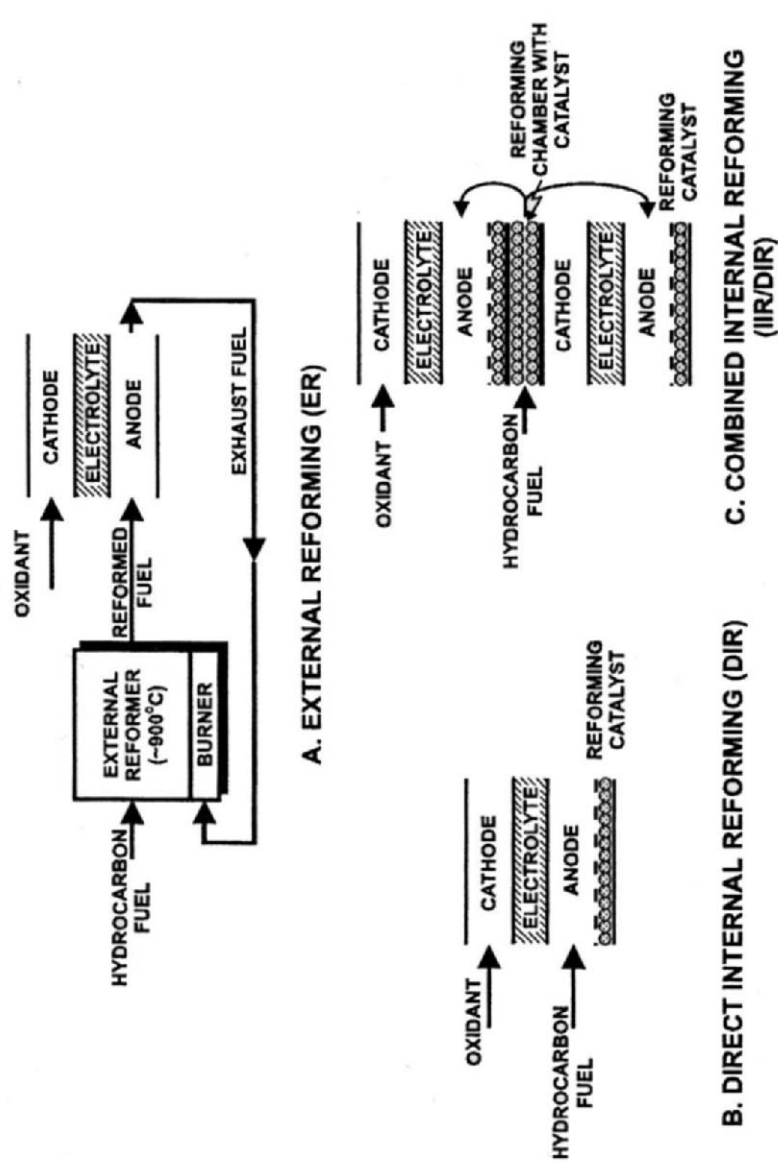


Figure 8.13. Process diagram for external, internal, and combined internal reforming of natural gas. Reprinted from Reference 10, Copyright (2001) with permission from Elsevier.

reforming in stacks, ranging in power levels from a few kW to 250 kW, has been demonstrated by Fuel Cell Energy. In some recent work at this company, both the IIR and DIR have been coupled, in an optimized manner, to attain the highest level of methane conversion, at a fuel utilization rate of over 70% in long-term lifetime studies.

Ansaldo Ricerche in Italy is in the process of developing an alternate configuration for the steam reformer, the *sensible-heat reformer* (SHR), to be closely integrated with the electrochemical cell stack.¹² The attractive features of the design are:

- good thermal management,
- low heat losses,
- low gas volumes, and
- minimal differential pressure between the internal/external sides of components.

Performance evaluations have been carried out at part-load and during load-following. The multifuel compatibility is also being tested.

SOFCs, like MCFCs, have also been developed for use with external and/or internal reformers. An advantage of the SOFC over the MCFC is that CO₂ recovery from the exit anode stream for feeding into the oxidant stream is not necessary. The SOFC only needs oxygen as the cathodic reactant, while the MCFC needs both O₂ and CO₂ to form the carbonate ion that transports the ionic current from the cathode to the anode. Most of the SOFC power plants developed to date are coupled with external steam reformers using natural gas. An interesting concept, invented by Siemens, was to use a pre-reformer at a relatively low temperature in the range of 250-500 °C to convert high molecular weight hydrocarbons, present in natural gas, to hydrogen.¹³ The exit gases methane, steam, and small amounts of hydrogen, CO₂, and CO from the pre-reformer were delivered to the anode chamber in the SOFC where internal reforming converted the methane to H₂ and CO. One advantage of this route was that the small amount of hydrogen from the pre-reformer maintained the anode electrocatalyst in a reduced state.

Siemens-Westinghouse have designed a natural-gas fuelled-pressurized SOFC system in order to attain high power densities and efficiencies. As illustrated in the schematic for this system (Figure 8.14), there are two stages for internal fuel-reforming and utilization, one operating at high pressures and the other at low pressures. Reforming occurs in the anode chamber and the heat required for the reaction is supplied by the anodic reaction. Steam is provided for internal reforming, as well as for preventing soot formation via a gas circulation loop. The NO_x emission level is only about 4 ppm. The fuel utilization mainly occurs at the anode. The overall efficiency of the hybrid system (fuel cell/gas turbine) to convert the chemical energy of the fuel to electrical energy is estimated at 67%, which is based on the lower heating value of the fuel.

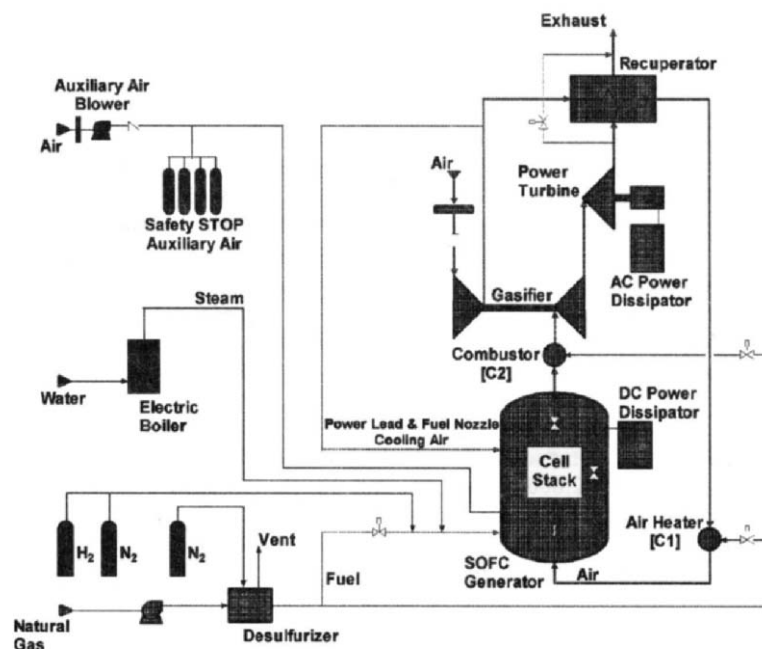
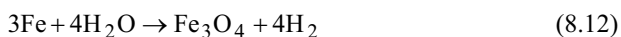


Figure 8.14. Schematic of a Seimens-Westinghouse hybrid-solid-oxide-fuel cell/gas-turbine-generator with internal reforming of natural gas. Reprinted from Reference 13.

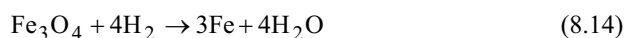
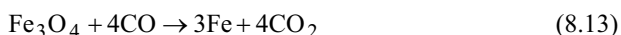
8.2.7. Coal Gasifiers for SOFC/Gas Turbine Hybrids, with H₂ Separation and CO₂ Sequestration

In recent years, several authors (Hendrik, Doctor, Simbeck, Spath, Williams, Kreutz et al.)¹⁴ have assessed the prospects for producing hydrogen and carbon monoxide from coal via gasification and for their utilization in gas turbine/SOFC hybrid power plants. It is technically feasible to capture CO₂ during hydrogen production. The CO₂ can then be compressed to supercritical pressures (> 10 MPa), transported by pipeline, and injected into underground storage sites (such as depleted oil or gas reservoirs or deep saline aquifers) for permanent sequestration. This would allow production of hydrogen from fossil fuels, with greatly reduced emissions of CO₂ to the atmosphere (Herzog et al.,¹⁵ Williams^{16,17}).

Another method of fuel processing involves the use of the *coal-steam-iron cycle* which is one of the oldest methods for hydrogen production. The reaction involved is:



Hydrogen, produced by this process is ultra-pure. Syngas, produced by the coal gasification reaction (Eq. 8.4) is utilized to regenerate the iron from the iron oxide, according to the equations:



The reader may be puzzled by the overall reaction, as written above. The overall reaction is the sum of the reactions (8.4), (8.12) and (8.13) and is expressed as:



i.e., the production of hydrogen from coal using steam as the second reactant. The use of the steam-iron reaction is one route to overcome the problem of impurities formed by the complete direct oxidation of coal. Instead, by use of the steam produced by reaction (8.4), the steam-iron reaction occurs. Reactions (8.13) and (8.14) produce iron in a spongy form with a high surface area. The coal-steam-iron cycle occurs at a temperature of 700-900 °C. One can also have a pressurized reactor. The fuel-cell company H Power proposed the steam-iron reaction for pure hydrogen generation and its utilization in a proton exchange membrane fuel cell. It was also suggested that the iron oxide could be generated at central sites, using syngas, produced from coal. The advantage of this method is that there will be no CO₂ emission from the fuel cell vehicle. The CO₂ removal at the central site could be sequestered to minimize atmospheric pollution.

For power generation, Steinberg and Cheng proposed a hybrid system,¹⁸ as illustrated in Figure 8.15. This scheme involves using a fraction of the hydrogen and carbon monoxide for combustion and the use of heat/steam in a gas-turbine/steam-turbine hybrid electric power generator to produce electric power. In this scheme, the steam-iron reaction is used to generate electricity from a fuel cell power plant.

8.3. HYDROGEN PRODUCTION FROM NUCLEAR AND RENEWABLE ENERGY RESOURCES

8.3.1. Role of Nuclear and Renewable Energy Resources

There is little doubt that the fossil fuels will be the major source of hydrogen in the near to intermediate term and also possibly in the long term, particularly if the technologies for carbon capture and sequestration are successfully implemented.

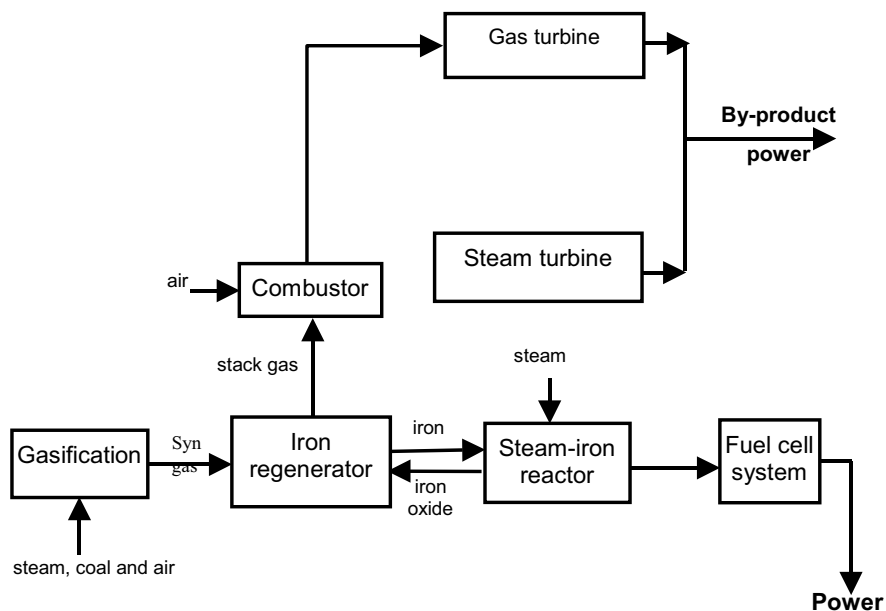


Figure 8.15. Coal-steam-iron cycle for ultra-pure hydrogen production and its utilization in fuel cells and for use of stack gas combustion for utilization in gas turbine/steam turbine. Reprinted from Reference 18, Copyright (1989) with permission from International Journal of Hydrogen Energy.

TABLE 8.1
Global Energy Resources^a

Source	Reserves plus resources, (thousand exajoules)
Primary Energy Resources^b	
Coal	199.7
Oil	32.4
Natural gas	49.8
Uranium	32.0
Renewable Energy Resources^c	
Hydro	0.05
Biomass	0.28
Solar	1.57
Wind	0.64
Geothermal	5.00

^a Extracted Reference 19

^b Data for primary-energy sources is for reserves plus resource base

^c Data for renewable-energy resources in thousands of exajoules/g

The main energy alternatives in the long term, will be to focus on renewable energy resources (see Table. 8.1). It is also necessary to examine the potential contribution of nuclear-energy resources, as shown in Table 8.1. This table clearly shows that nuclear and solar energies could be the winners to displace fossil fuels. Even though at the present time there are countries like France and Belgium that are strongly dependent on nuclear power, the strong antinuclear lobby and safety considerations have recently retarded the growth of nuclear power. Solar power can solve the world's energy problems but due to the requirement of large areas of land, the high cost of solar power and the need for extensively coupled energy storage systems, the growth rate has been slow. The other renewable energy sources—hydro, wind, geothermal, tidal, and biomass—are site specific in respect to their availability, but will still have some role in contributing to the energy sector.

With all the renewable energy resources, the main focus has been on electricity generation. Another important aspect is the vital need of a liquid or gaseous fuel for applications such as transportation and portable power. The ideal fuel, which will meet this demand and provide a solution to the global warming problem, is hydrogen. In the following Sections, we shall deal with the methods of the production of hydrogen using the renewable energy resources.

8.3.2. Water Electrolysis

8.3.2.1. *Thermodynamic and Electrode Kinetic Aspects.* Water electrolysis is one the simplest and best known technologies for hydrogen production, whether it is on a small or large scale. The overall reaction is the decomposition of water into its components:



It is exactly the reverse of this reaction which occurs in a fuel cell. The standard free energy change and enthalpy change have values of 236.83 kJ/mol and 285.58 kJ/mol, respectively, for the case of liquid water being the reactant and the products being gases at a pressure of 1 atm and temperature of 25 °C. The decomposition of water is an energy driven reaction, while the fuel cell reaction is a spontaneous one. During water electrolysis, electrical energy is supplied from a power source for this reaction. As stated in Chapters 1 and 2, the thermodynamic reversible potential (at 25 °C and 1 atm pressure of reactant gases) for the reaction is 1.229 V. Thus, this is the minimum voltage that can drive a water electrolysis cell. However, since the entropy change (ΔS) for the reaction is negative, the electrolysis cell will absorb heat from the surroundings if water electrolysis is carried out at a potential between the thermodynamic reversible potential and thermoneutral potential (E_t) of 1.484 V (this potential corresponds to the enthalpy change of the reaction $\Delta H^0 = -nFE_t$.) Other factors, which have to be taken into consideration, are the activation overpotential losses at the anode and cathode and also the ohmic overpotential losses, mainly in the electrolyte. Mass transport overpotential losses are minimal

during water electrolysis. Thus, the cell potential (E) vs. current density (i) relation for water electrolysis can be expressed by the equation:

$$E = E_r + b_a \ln \frac{i}{i_{o,a}} + b_c \ln \frac{i}{i_{o,c}} + iR \quad (8.17)$$

where E_r is the reversible potential, i_0 's are the exchange current densities (the suffixes a and c denote anodic and cathodic reactions, respectively), and R is the internal resistance of the water electrolysis cell. As in the case of fuel cells, the slow kinetics of the oxygen electrode reaction causes high activation overpotential losses at the desired current densities.

Taking into consideration the expressions for the variation of the reversible potential with temperature and pressure (see Chapter 1), from a thermodynamic point of view it is more favorable to operate water electrolysis cells at high temperatures and low pressures. However from a technological point of view, high temperatures and high pressures are most beneficial in (i) enhancing the electrode kinetics of the reactions, (ii) reducing ohmic overpotential, and (iii) minimizing energy requirements for compression and storage of product gases.

The efficiency of a water electrolyzer (ε) may be defined by the equation:

$$\varepsilon = \frac{\text{Chemical Energy Output}}{\text{Electrical Energy Output}} = \frac{\Delta H}{nFE} \quad (8.18)$$

The assumption made in this equation is that the coulombic-current efficiency for water electrolysis is unity. This is practically always the case. If water electrolysis is carried out at a cell potential of 1.48 V, the thermoneutral potential, the efficiency is 100%. Invariably, the activation overpotential at the anode and the ohmic overpotential in the cell raise the E values to more than 1.6 V (typically about 1.8 V) and thus, the practical efficiencies are in the range of 75 to 90%.

Another important factor has to be taken into consideration in ascertaining the efficiency of hydrogen production using a water electrolyzer, i.e., the efficiency for electric-power generation from the primary energy source. This efficiency is about 30 to 35% for a thermal power plant, when using coal or oil, and may be as high as 50% for a combined cycle gas turbine power plant using natural gas. Using these values and assuming the efficiency of the water electrolysis plant to be about 80%, the overall efficiency for hydrogen production from the fossil fuels via the water electrolysis route will be in the range of 35 to 45%. It is for this reason that the chemical route of fuel processing is preferred for the large-scale production of hydrogen (Section 8.2). For a smaller scale production—as for instance in the semiconductor industry where ultra-pure hydrogen is required—the water electrolysis route is more economical.

Entering the non-fossil renewable energy resource era, hydrogen production by water electrolysis will be, most probably, the most techno-economically feasible

route. Efficiencies for hydrogen generation will be considerably higher with the hydroelectric and wind-generator power plants than with the nuclear or photovoltaic power plants. The costs of such power plants may play an overriding role in determining the cost of hydrogen generation.

8.3.2.2. *Types of Water Electrolyzers and Status of Technologies.*

Three types of water electrolyzers have been developed on the type of electrolyte used: alkaline, proton-exchange membranes, and solid-oxide electrolytes.

The most commercialized one is that with an alkaline (6–8 N KOH) electrolyte. In this case too, there is a further classification: monopolar (tank-type cells) and bipolar (filter-press type cells). Figure 8.16 illustrates the fundamental difference in design of the two types of alkaline water electrolyzers.²⁰ In the monopolar design, the cells in a stack are connected externally in a series/parallel arrangement, while in the bipolar design, a bipolar plate serves as a current collector for the anode on one side and for the cathode on the other (the latter is just as in the case of all types of fuel cells except that for the solid oxide water electrolyzer). The advantages of the bipolar design is that electron flow during electrolysis from one cell to the next is across the whole bipolar plate and ohmic losses are thus minimal. In the unipolar design the current flow is in the longitudinal direction in the electrodes, and thus, the ohmic losses are higher. In the former case, it is possible to attain higher current densities at the same cell voltage.

Significant advances have been made in optimizing the structure and composition of the electrode to minimize activation and ohmic overpotentials in alkaline-water electrolyzers. Noble metals or their alloy electrocatalysts are not required in the alkaline environment. Nickel-based electrocatalysts are mostly used for the oxygen evolution reaction. By use of lithium-doped nickel oxide, nickel cobalt spinel (NiCo_2O_4), and perovskite ($\text{Ni}_{0.2}\text{Co}_{0.8}\text{O}_3$), anodic overpotentials are decreased and more importantly, the degradation in performance with time, caused by oxidation of Ni^{3+} to Ni^{4+} , has been minimized. For the hydrogen electrode, high surface area nickel or stainless steel are used as electrode materials. The activation overpotential at this electrode is reduced by use of NiB, Ni-S, Ni-Al, Ni-Mo, or NiCo_2S_4 thiospinel electrocatalysts. Further, by the use of these compound materials, degradation due to hydrogen entry into nickel, which causes embrittlement problems, are minimized. Even though in the early times of technology the unipolar electrolyzers were the more common ones, in more recent times the transition has been to bipolar electrolyzers. Alkaline water electrolyzers are generally operated at about 70 to 80 °C. Operation under pressure is desirable to minimize energy requirements. Such a large scale electrolyzer of this type, which has been commercialized, was manufactured by Lurgi.

Table 8.2 presents the operating characteristics of the well-developed water electrolyzers. It also includes the operating characteristics of the novel proton-exchange-membrane water electrolyzer (PEMWE), formerly referred to as the solid-

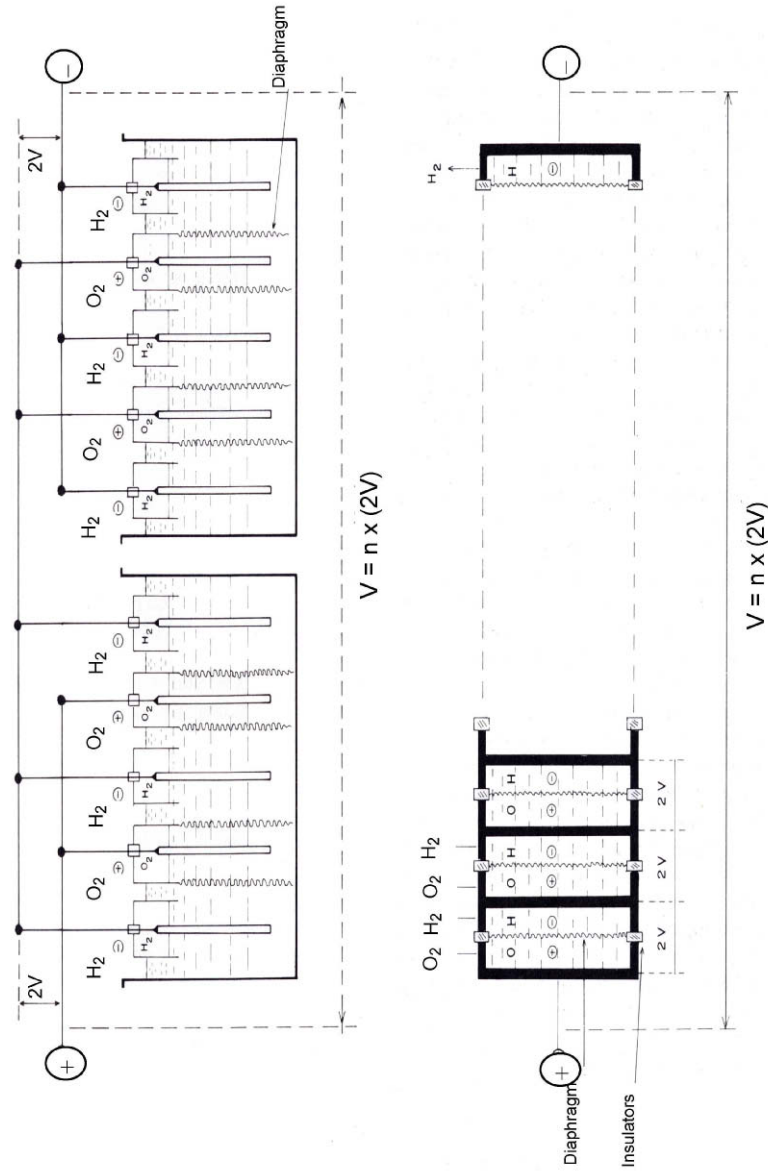


Figure 8.16. Design of cell stacks in water electrolyzers (a) unipolar (b) bipolar. Reprinted from Reference 20, Copyright (1981), with permission from Plenum.

TABLE 8.2
Operating and Performance Characteristics of Water Electrolyzers^a

Manufacturer	Brown Boveri and Cie	Denora SPA	Lurgi GmbH	Norsk Hydro A.S	The Electrolyzer Corp. Ltd.	Krebskosmos	Teledyne Energy Systems	G.E's SPE
Cell type	Bipolar filter press	Bipolar filter press	Bipolar filter press	Bipolar filter press	Monopolar tank	Bipolar filter press	Bipolar filter press	Bipolar filter press
Operating pressure (atm)	Ambient	Ambient	32 atm	Ambient	Ambient	Ambient	2.4 atm	3.9 atm
Operating temperature (°C)	80	80	90	80	70	80	82	80
Electrolyte	25% KOH	29% KOH	25% KOH	25% KOH	28% KOH	28% KOH	35% KOH	DuPont Nafion-1200 EW
Current density (A/m ²)	2000	1500	2000	1750	1340	3000	2000	5000
Cell voltage (V)	2.04	1.85 (increases to 1.95 after 2 y)	1.86	1.75 (after 1 yr. operation)	1.90	1.90	1.90	1.70
Current Efficiency (%)	>99.90	~98.50	98.75	>98.00	>99.90	>99.9	-	-
Oxygen Purity (%)	>99.60	99.60	99.30-99.50	99.30-99.70	99.70	99.50	>96.00	>98.00
Hydrogen Purity (%)	>99.80	99.9	99.80-99.90	98.80-99.90	99.9	99.9	99.99	>99.00
Power Consumption (DC-kWh per normal m ³ H ₂)	4.90	4.60	4.50	4.30	4.60	4.50	6.00	4.10

^aReprinted from Reference 1, Copyright (1985) with permission from John Wiley and Sons.

polymer-electrolyte water electrolyzer. This technology was a spin-off of General Electric Company's proton exchange membrane fuel cell technology. A schematic of the single cell in a PEMWE is illustrated in Figure 8.17. The compact design with a thin electrolyte (Nafion) layer and an electrode structure permits the ready escape of evolved gases through the electrodes to the flow channels in the bipolar plate. Ohmic overpotential problems due to gas bubble formation (commonly encountered in alkaline-water electrolyzers) are thus minimized. This makes it possible to attain current densities two to three times higher at the same cell voltage in PEMWEs than those in AWEs and in solid-oxide electrolyte water electrolyzers (see Figure 8.18). The PEMWEs are capable of generation rates of 1 A/cm^2 for hydrogen and oxygen, at a cell potential of 1.8 V. Since the electrolyte in the PEMWE is acidic, it is necessary to use noble metal-based electrocatalysts. Platinum is the best electrocatalyst for the hydrogen evolution reaction while a mixed

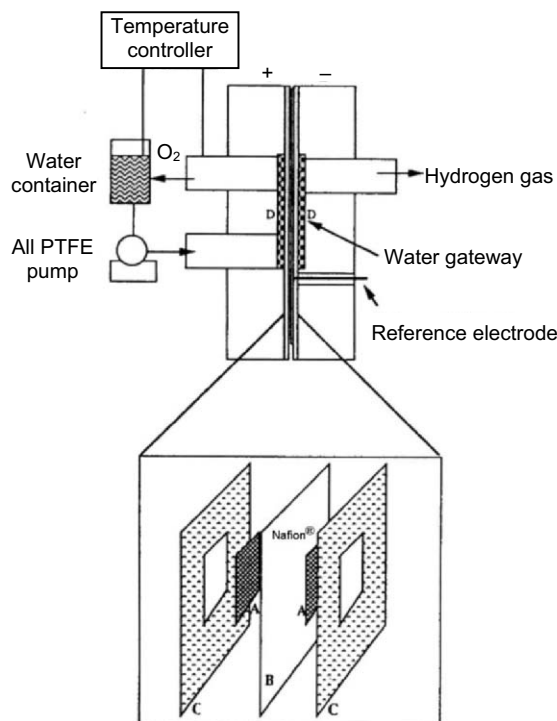


Figure 8.17. A design for a single cell in a proton exchange membrane water electrolyzer. Reprinted from Reference 23, Copyright (1993) with permission from Elsevier.

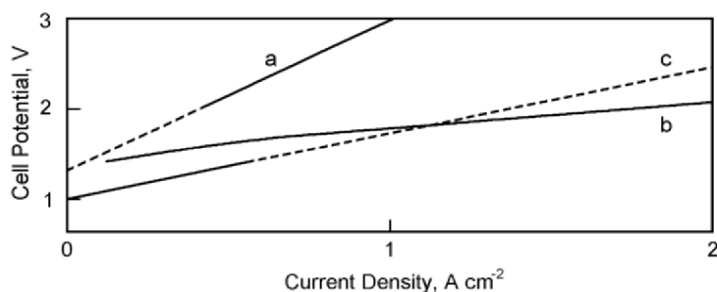


Figure 8.18. Typical cell potential vs. current density plots for (a) alkaline, (b) proton exchange membrane, and (c) solid oxide electrolyte water electrolyzers.

oxide electrocatalyst with the composition of $\text{RuIr}_{0.5}\text{Ta}_{0.5}\text{O}_x$ with $x = 2$ was found to be the best one for oxygen evolution.^{21,22} These electrocatalysts are electrodeposited or vapor deposited on a metallic substrate. Fine titanium mesh was used for this purpose. Just as in the case of PEMFCs, the electrodes were impregnated with a proton conductor (e.g., Nafion) to extend the three-dimensional reaction zone.

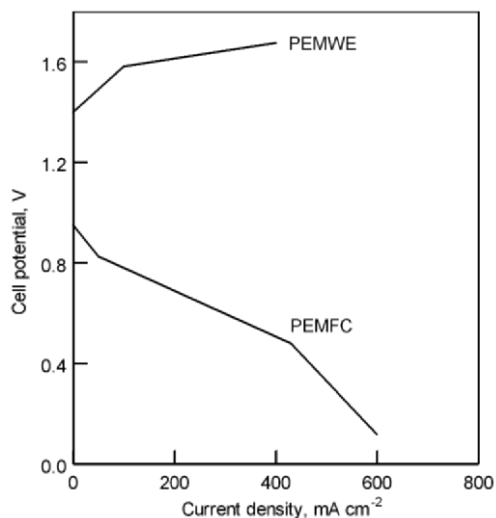


Figure 8.19. Cell potential vs. current density plots for a regenerative proton exchange membrane water electrolyzer (PEMWE)/fuel cell (PEMFL).

An added attraction of the PEMWE is that it can also be used in the reverse mode as a fuel cell, i.e., the system would function as a regenerative fuel cell. The cell potential vs. current density performances in both modes, as obtained in a recent research investigation,²³ is shown in Figure 8.19. In the fuel cell mode, it was better to use the RuIrTaO_x electrocatalyst for the hydrogen oxidation reaction and the Pt electrocatalyst for oxygen reduction. Since the electrode structures were not optimized, the performance in the fuel cell mode was considerably less satisfactory than in the state-of-the-art PEMFCs. Giner Inc. has reported²⁴ the development of a unique, highly-efficient, bifunctional oxygen electrode structure that shows similar performance to the typical, efficient discrete PEMWE and PEMFC oxygen catalysts. Round trip electrical efficiency (PEMFC voltage/PEMWE voltage) for a single unit regenerative fuel cell with this structure is approximately 46% at 500 mA/cm², 80 °C, ambient pressure. The General Electric Technology was sold to the Hamilton Standards Division of United Technologies Corporation in the 1980s. Since then, the latter company has had contracts from NASA to develop PEMWEs and Regenerative fuel cells.

The third type of water electrolyzer with a solid oxide electrolyte, was developed by Brown, Boveri (presently ABB)²⁵ and Dornier.²⁶ Just as in SOFCs, the electrolyte is ZrO₂-Y₂O₃. Nickel was used for the cathode electrocatalyst and LaMnO₃ doped with Sr for the anode electrocatalysts. Advantages of operation at 1000 °C are: (i) the thermodynamic reversible potential is about 200 mV less than at below 100 °C; (ii) the temperature effect on the kinetics of the electrochemical reactions greatly reduces the activation overpotentials; and (iii) since the system is a two phase (solid-vapor system), the same cell can be used in both modes (fuel cell/water electrolysis). The net result is that the overall efficiency for the regenerative system can be as high as 70%, just as in the case of rechargeable batteries. Water vapor electrolysis appears attractive because of the considerable decrease in the thermodynamic reversible potential by about 0.2 to 0.3 V at 1000 °C, as compared with that at 80 °C, as well as for the significantly higher exchange current densities for hydrogen and oxygen evolution. However, it presents several drawbacks. First, it needs process heat to evaporate the water and maintain the cell temperature because of the positive value of the entropy change, and if the cell potential is less than the thermoneutral potential, the cell will cool. Also, there is a requirement of thermally stable and compatible materials for the cells and cell stacks. Finally, it needs the use of sophisticated and expensive fabrication techniques for the cell stacks, as in the case of SOFCs (see Chapter 4).

8.3.3. Photoelectrolysis

The first demonstration of this method of hydrogen production was by Fujishima and Honda, who used a single crystal TiO₂ anode electrocatalyst and a platinum cathode electrocatalyst.²⁷ In a photoelectrochemical cell, an interface of a n-type semiconductor with an electrolyte was illuminated with light energy above

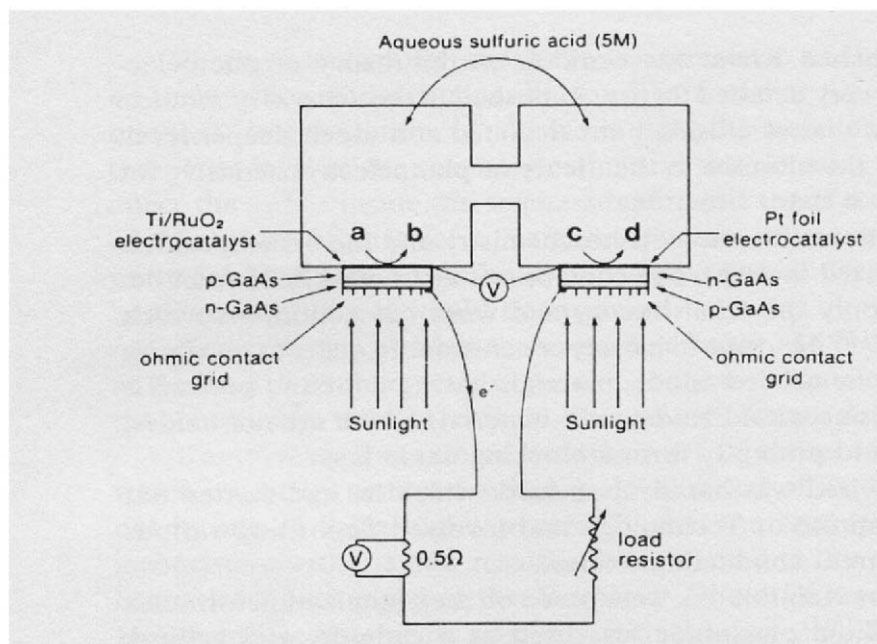


Figure 8.20. Schematic of a photoelectrochemical cell for production of hydrogen.

the band-gap of the material (Figure 8.20). This caused the transport of electrons toward the bulk of the semiconductor and holes towards the surface (the photoanode). The opposite behavior is observed at the photocathode. Thus, light promotes photoreduction at p-type semiconductors and photooxidation at n-type materials. One factor, which must be taken into consideration, is that the splitting of water requires an energy input of 285.58 kJ/mol of H_2 (2.96 eV). Thus, it is necessary to use a semiconductor material with a band-gap of at least 3 eV at one of the electrodes (e.g., TiO_2) to produce two moles of H_2 and one mole of oxygen. But at this band gap the material can capture only the ultraviolet light from the solar spectrum, which corresponds to about 2% of the solar energy. Thus, attempts were made to achieve a higher response to solar radiation by the use of sensitizers and dye molecules (e.g., ruthenium 2-2'-bipyridine). These molecules capture the incident sunlight, producing excited states that inject charge carriers into the conduction band of the semiconductor.

A stand-alone photoelectrolysis cell with a reasonably good efficiency was first demonstrated by Kainthala et al.²⁸ (see Chapter 1 and Figure 1.5). The semiconductor materials used for the electrodes were a Pt-catalyzed indium-phosphide cathode and a MnO_2 coated gallium-arsenide anode (the MnO_2 coating

was to prevent electrooxidation). An overall efficiency of about 8% was obtained. More recently, values of 16% have been claimed, making this approach potentially better than the dual approach of using photovoltaic/electrolysis cells to decompose water. However, problems in photoelectrochemical cells are most challenging because of the needs of very large area electrodes, circulation of the electrolytes, and auxiliary requirements for thermal management. On the contrary, the technology for manufacturing photovoltaic cells, producing kW to MW electric power has been demonstrated, and these systems can be readily coupled with large water electrolyzers, which are already available (see Section 8.3.2). Thus, there is only an academic interest in methods to enhance the efficiencies of photoelectrochemical reactions using (i) dye sensitizers, (ii) electrocatalysts for recombination of the H and/or O atoms produced in the electrochemical reactions, and (iii) alternate reactions with redox couples to lower the band-gap requirements for photosplitting of the reactant molecules (e.g., HBr or HI).

8.3.4. Thermochemical Decomposition of Water

In the 1970s, there was great interest in hydrogen production using thermal energy, particularly utilizing the high-grade waste heat energy from thermal power plants as well as from chemical plants. It was stated in the preceding Section that the dissociation energy for the decomposition of abundant liquid water into its constituents is 285.58 kJ/mol H_2 . At any temperature, water is in equilibrium with hydrogen and oxygen according to equation 8.12. The equilibrium constant for this reaction is expressed by:

$$K = \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \quad (8.19)$$

The extent of the thermal dissociation of water as a function of temperature is shown in Figure 8.21. For a complete dissociation in a stand-alone system, a temperature of about 4000 K is required. Further, it will be necessary to separate the product gases, for instance by using some selective membranes.

The concept of a thermochemical cycle for water decomposition was proposed so as to employ different schemes for the intermediate steps. Those having positive entropies are driven at higher temperatures and the intermediate steps having negative free energies at lower temperatures. Thus, if the first reaction has a positive entropy change, the second reaction may occur with a more favorable reaction rate at the same or preferably lower temperatures. Several thermochemical cycles have been researched for hydrogen production. As an example, a route to hydrogen production is:

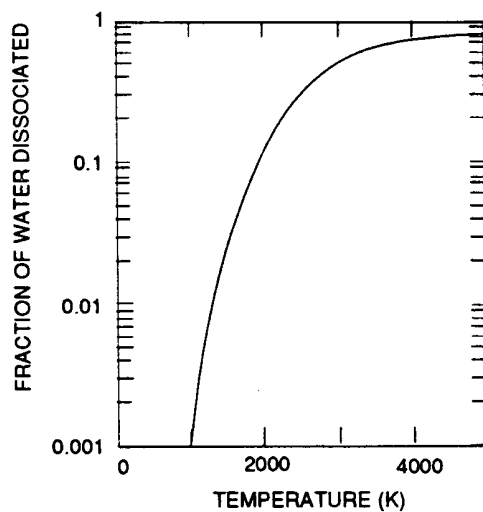
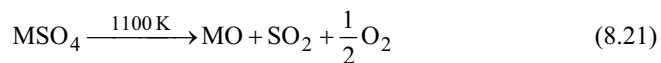


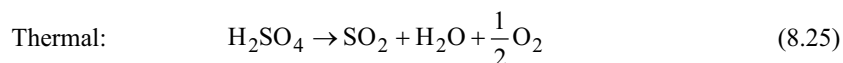
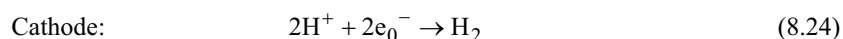
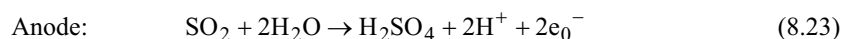
Figure 8.21. Dissociation of water as a function of temperature.



where M is a metal, like iron. The theoretical efficiency of a thermochemical cycle is limited by the Carnot efficiency. However, because at least one of the intermediate steps is carried out at a high temperature, high values for efficiency could be predicted. Further cost of chemicals used in several thermochemical cycles (e.g., $\text{Fe}_2\text{O}_3/\text{FeSO}_4$, $\text{FeCl}_2/\text{Fe}_3\text{O}_4$, HI/SO_2 , CaO/I_2 , CaBr_2) are quite low, and there is a considerable use of inexpensive heat energy rather than expensive electrical energy as needed for water electrolysis for hydrogen production. Thus, there were many research programs in the USA, Russia, Germany, and Japan in the 1970s and early 1980s to develop such systems but the prospects of using this technology were found to be bleak due to the following reasons:

- (a) Carnot limitations makes it difficult to attain more than two thirds of theoretical efficiency;
- (b) high efficiencies, on the basis of thermodynamics, could not be attained in practical systems, because of kinetic constraints;
- (c) several of the intermediate chemical reactants or products rapidly corrode reaction vessels at the high temperatures required for at least one of the steps in the overall cycle;
- (d) energy requirements for pumping and product gas separation are high; and
- (e) loss of chemicals because of lack of complete cyclicity.

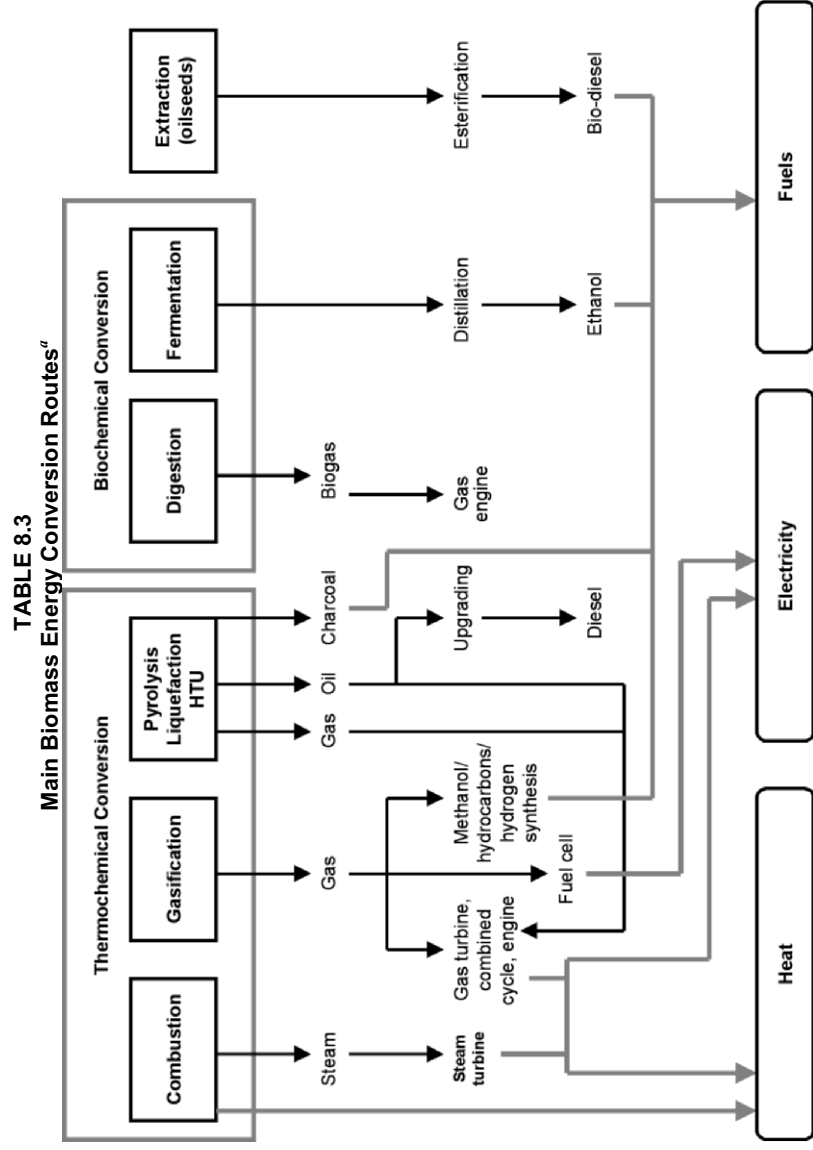
An alternate route that appeared more promising is the thermochemical-electrochemical hybrid cycle, extensively investigated by the Westinghouse Electric Corporation. It has the following intermediate steps:



In the electrochemical cell, akin to a water electrolysis cell, hydrogen is evolved at the cathode and SO_2 is oxidized to H_2SO_4 . The latter reaction occurs instead of the oxygen evolution reaction, which requires a considerably higher voltage (about 1 V). Lowering the cell potential by using SO_2 instead of water as the anodic reactant is thus possible because of the significant difference in the thermodynamic reversible potentials for the SO_2 oxidation and oxygen evolution reaction. Sulfuric acid is produced at a concentration of about 80%. It is then vaporized to form SO_3 and H_2O , and SO_3 is decomposed catalytically to SO_2 and O_2 in a thermal reactor. Even though there is some overpotential associated with the SO_2 oxidation in the electrochemical cell, Westinghouse estimated a decrease in electric energy consumption by 40% using this hybrid cycle instead of water electrolysis.

8.3.5. Biomass Fuel Production and Conversion to Hydrogen

Biomass energy resources are derived from plants, trees, and crops, as well as from agricultural and forest residues and organic waste-streams. According to the World Energy Assessment (WEA) in the United Nations Development Program (UNDP), the contribution of biomass to the world's total energy supply (electricity, heat, and fuels) is about 9.13% (45 ± 10 exajoules per year). The main biomass energy conversion routes, as described in UNDP's WEA, are illustrated in Table 8.3.



^aReprinted from Reference 19.

The focus of this Section will be on the production of H_2 and of H_2 plus CO for utilization in PAFCs, MCFCs, and SOFCs.

Table 8.3 presents several routes, thermal gasification, pyrolysis, liquefaction, anaerobic digestion, fermentation, or extraction of oil seeds for production of gaseous-liquid hydrocarbon or alcohol fuels. Most of these fuels can be processed to produce hydrogen or hydrogen plus carbon monoxide for subsequent utilization in fuel cells. Alternatively, the fuels could be used in thermal engines (gas turbines, IC engines, diesel engines). In some countries (Scandinavian countries, India, China) where biomass derived fuels are extensively used for combined electricity and heat production, the most efficient method is the biomass-integrated-gasifier/combined-cycle gas turbine. For the fuel cell application, H_2 or H_2 plus CO production involves the sequence of steam reforming and the two-stage shift conversion (see Section 8.2.3). If pure hydrogen (purity of 99.99%) is required, as for PEMFCs or AFCs, the pressure-swing absorption method (see Section 8.2.1) can be used.

Even though there are several routes (Tables 8.3) for production of biomass derived liquid or gaseous fuels, the fuel cell community has concentrated on the processing of biomass derived gaseous or liquid fuels produced either by biomass gasification or anaerobic digestion. However, the fuels produced by the other methods shown in Table 8.3 could also be similarly processed. Biomass gasification produces syngas. Fluidized bed gasifiers are generally used for large-scale syngas production. It is preferable to use oxygen rather than air for the gasification, because the latter method produces a high amount of nitrogen. The product gas must be cleaned up before use for hydrogen or hydrogen plus carbon monoxide production. Particulate matter is removed using a cyclone separator, and water quenching removes small particles, condensable hydrocarbons, alkali compounds, and ammonia. Fabric filters can be used for eliminating sub-micron particles. A zinc oxide bed can capture sulphur compounds.

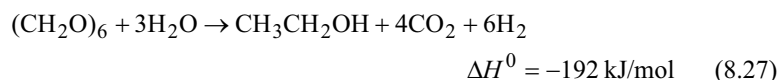
8.3.6. Biological/Biochemical Production of Hydrogen

Several methods have been proposed and investigated for the biological/biochemical production of hydrogen. These will be briefly summarized as follows:

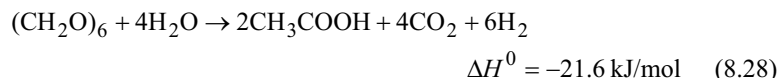
- (a) *Use of photosynthetic catalysts.* In this approach, hydrogen is generated from water and sunlight using photosynthetic catalysts such as heterocystous blue-green algae. The algae contain the enzyme hydrogenase, which catalyzes the photochemical decomposition of water to produce hydrogen. This reaction is inhibited by the formation of oxygen in the reactor. Efficiencies of only 3% have been achieved. Since the biochemical production also occurs at low temperatures, this method may be useful for only low rates of hydrogen production.
- (b) *Anaerobic Digestion.* This method can produce a variety of biochemicals from vegetable and animal wastes using fermentative and acetogenic bacteria. The fermentative bacteria can cause a breakdown of several

biochemicals, as for example polysaccharides into sugars; proteins into peptides and amino acids; fats into glycerine and fatty acids; and nucleic acids into nitrogen heterocyclics ribose and inorganic phosphates. The acetogenic bacteria cause a further breakdown of the sugars, alcohols, and higher acids into acetic acid, hydrogen, and water. Typical reactions may be represented by:

Fermentative bacteria:



Acetogenic bacteria:



These reactions are not inhibited by the presence of oxygen. Using this approach, the hydrogen generation occurs at low efficiencies and at low rates. This approach for hydrogen production is far fetched because (i) it requires large land requirements, (ii) the hydrogen generation rates are low, and (iii) capital costs are prohibitive. There may be some applicability in remote rural areas where the power requirements will be low.

8.4. OTHER FUELS FOR DIRECT OR INDIRECT UTILIZATION IN FUEL CELLS

8.4.1. Partially-Oxygenated Carbonaceous Fuels

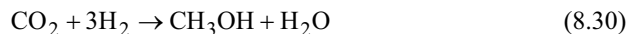
8.4.1.1. *Methanol and Ethanol.* Hydrogen is the most electroactive fuel for low and intermediate temperature fuel cells (PEMFC, AFC, PAFC), while H_2 or H_2 plus CO are the most electroactive for the high temperature fuel cells. Even in the latter case, it is very possible that CO, along with steam, undergoes the water gas shift reaction on the anode electrocatalyst and the half-cell reaction at this electrode is the electro-oxidation of hydrogen. During the 1960s, there was great

interest in the direct utilization of saturated and unsaturated aliphatic hydrocarbons in, predominantly, phosphoric acid fuel cells. However, in practically all these cases, the exchange current densities for their electro-oxidation were found to be extremely low, even considerably lower than for the cathodic reduction of oxygen. The reason for this is the difficulty of breaking up the C-H, and more so the C-C bonds, in these hydrocarbons. Since the 1970s, progress has been made at the Energy Research Corporation (recently with a name change to Fuel Cell Energy) in the direct utilization of natural gas in MCFCs and more recently this approach has been investigated in SOFCs. In these cases, the anode electrocatalyst (or sometimes a second catalyst behind this one in the electrode) first performs the steam-reforming reaction and perhaps the shift-conversion reaction and then the H_2 or H_2 plus CO are electro-oxidized at the anode.

The alternate approach in the 1960s was to investigate partially oxidized organic fuels for direct utilization in fuel cells. From that period until the present time, methanol has been found to be the most electroactive organic fuel. It has been found to be relatively easy to dissociatively adsorb methanol on a platinum electrocatalyst but somewhat challenging to further electrochemically oxidize these adsorbed species to carbon dioxide and water. The details of the electrode kinetics and electrocatalysis of electrooxidation of methanol are presented in Chapter 4, Section 4.3. Since the early 1990s, there was more success in developing DMFCs, with perfluorosulfonic acid membranes, rather than with sulphuric acid, as the electrolyte as had been previously used from the 1960s (see Chapter 4). Another partially oxidized hydrocarbon fuel of great interest for fuel cell application is ethanol. Both methanol and ethanol are liquid fuels, like gasoline, and have about 50% to 60% of the energy density of the latter fuel. Thus, they are appealing fuels for the transportation application. The difficulty of the direct utilization of ethanol in fuel cells is because even though it dissociatively adsorbs on the platinum electrocatalyst, it is difficult to break up the C-C bond. Further, in low temperatures fuel cells, it is only partially oxidized to acetic acid. However, according to a recent study,²⁹ it was shown that at about 140 to 150 °C, there is complete electro-oxidation of ethanol to CO_2 and H_2O in a direct-ethanol fuel cell with a Nafion/silicon oxide-composite proton-exchange membrane (see Chapter 4). Another partially oxidized fuel of some interest was glucose for biomedical applications, e.g., as a fuel-cell power-source for pacemakers or artificial hearts. The electroactivity of this fuel was far less than that of methanol or ethanol. In the remainder of this Section, we shall make some brief comments about the production of methanol and of ethanol, (partially-oxidized organic fuels) to be used directly or indirectly in fuel cells.

The largest application of methanol is in the plastics industry and on a large scale it is produced predominantly in the USA from natural gas by first steam reforming it to CO and H_2 (Eq. 8.1), and then, by the reaction of these two gases on a catalyst to produce methanol (Eq. 8.3). For this reaction, the pressure is 60-80 atm, the catalyst is CuO-ZnO, and the desired operating temperature is 250-280 °C. During the steam reforming of methanol, CO_2 is also formed, and this gas can also

be converted to methanol. An effective catalyst for methanol production by this route is:



This reaction increases the yield of methanol production.

Another largely available primary energy source for methanol production is coal. In this case, syngas is first produced by the reaction represented by Eq. (8.4), and this reaction is then followed by the one expressed by Eq. (8.3). Since the reaction producing methanol is exothermic, the reactors are designed to have efficient cooling by water circulation. In some cases, cooling is affected by feeding cold synthesis gas and having heat exchangers.

A third approach for methanol production is from biomass. Biomass is a renewable, clean feedstock with less environmental problems than coal. The major problem is their scattered availability. Liquid fuels can be obtained from biomass by pyrolysis, direct liquefaction, or by converting biomass, first to syngas and then to methanol (Eq. 8.3).

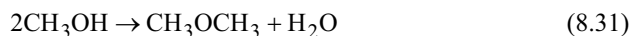
In respect to economics, the cost of methanol production on a large scale is lowest when natural gas is used as the primary energy source. It is somewhat higher from coal and still higher from biomass. The lowest cost of methanol production is about twice that of gasoline, based on an energy equivalent basis.

Ethanol is mainly produced on a large scale by fermenting sugars in sugar cane, maize, and corn. The countries noted for large-scale production of ethanol are Brazil, France, the USA, and Zimbabwe. The total amount of ethanol produced worldwide is about 20 billion liters (≈ 450 petajoules). The fermentation process involves the breakdown of the sugars in very much the same way as for the production of wines, using organisms such as yeast and bacteria. The biocatalysts for the reactions are acids or enzymes, commonly referred to as amylases or xylanases. The advantages of biological processes are their high specificities for the production of desired products from the biomass. Further, these processes occur at ambient temperatures and pressures. One problem is that the costs of production of such fuels are higher by about a factor of two, compared to the costs of production of gasoline and diesel fuel from petroleum resources. This is the reason for the gradual decrease in the manufacture of alcohol-fueled automobiles in Brazil, which was at the highest level in the 1980s. Nevertheless, with the great concerns of dependence on foreign oil, the environmental pollution problems from automobiles, and the steadily decreasing economic situation of farm workers, there is still interest in ethanol as a fuel for the transportation application. Further, because of the increasing prospects of developing direct-ethanol fuel cells (DEFCs) operating at intermediate temperatures, there is some hope for utilization of this potentially abundant fuel directly in fuel cells.

8.4.1.2. Dimethyl Ether (DME). During the last 4 to 6 years, there has been interest in using dimethyl ether as a fuel directly in diesel engines for

transportation application and in fuel cells. DME, like methanol or ethanol, is a clean fuel; since it is also a partially oxidized fuel, it undergoes complete combustion to carbon dioxide in a thermal engine. In a compression-ignition diesel-injection (CIDI) engine, DME has a high cetane number and the tail-pipe emissions are extremely low, unlike in the case when diesel fuel is used. It has also been recently demonstrated that in a proton-exchange-membrane fuel cell, DME has about the same level of electrochemical activity and yields CO_2 and water as its main production of electro-oxidation.³⁰ Since DME is a gas at room temperature (its boiling point is -25°C), it has to be stored at a pressure of about 10 bar, i.e., somewhat the same as for liquid propane gas.

Just as in the case of methanol, DME can be produced from natural gas or syngas. The reactor is practically the same as that for methanol production except that it also contains a solid dehydration catalyst for the reaction:



By selecting the operating conditions, the extent of coproduction of dimethyl ether and methanol can be varied over a wide range (5 to 95%).

At the present time, DME is mainly used as an alternative to chlorofluorohydrocarbons (CFCs) in aerosol sprays. Unlike in the case of CFCs, DME does not affect the ozone layer. It is also non-toxic and non-carcinogenic. Other uses of DME are in the synthesis of oxygenated hydrocarbons (e.g., methyl acetate) and higher hydrocarbon ethers. DME is also used as an intermediate in the Mobil MTG process for the production of gasoline from methanol. The companies, Haldor Topsoe and Amoco, estimate that if low cost natural gas is available, DME can be produced at costs comparable to that of diesel fuel.

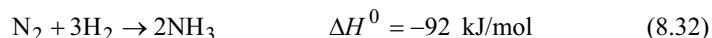
8.4.2. Nitrogenous Fuels

8.4.2.1. General Comments. The nitrogenous fuels ammonia and hydrazine have hydrogen contents comparable to gaseous, liquid, or solid hydrogen fuels (see Section 8.5.1). Ammonia is widely used by the agricultural industry for the production of fertilizers. It has also been used as the fuel for farm vehicles powered by internal combustion engines. It is difficult to electrooxidize ammonia completely to N_2 and water in fuel cells. A partial oxidation product is hydroxyl amine. However, there has been interest in using ammonia as a storage medium for fuel cells. The hydrocracking of ammonia can be carried out in a relatively simple fuel processor at a temperature of 450°C and at a pressure of 10 bar. The product hydrogen can then be used in a fuel cell.

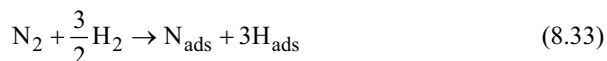
Hydrazine is a rocket fuel. It is electrochemically active in a fuel cell. The accepted view is that in an alkaline fuel cell, hydrazine is decomposed to nitrogen and hydrogen and the hydrogen is then electrooxidized at the anode. Since hydrazine is a liquid with a relatively high solubility in water, it is necessary to have a separator in the fuel cell to prevent its diffusion to the cathode, where it causes

depolarization. The following Sections will deal briefly with the synthesis of ammonia and of hydrazine.

8.4.2.2. Ammonia. Ammonia is synthesized on a large scale for the agricultural industry by the Haber process. In the USA, the primary reactants are natural gas and nitrogen. Natural gas is first converted to hydrogen by the steam reforming and shift conversion reactions, followed by the methanation or pressures swing absorption methanol for its purification (see Section 8.1). Hydrogen and nitrogen (separated from air by liquefaction) are reacted using iron as the catalyst, in the well-known Haber process for the large scale production of ammonia, according to the following reaction:



The number of moles in the reactant mixture is reduced during product formation and thus the reaction is exothermic. According to Le Chatelier's principle, higher pressures and lower temperatures accelerate the reaction rate. Industrial production of ammonia is carried out in the pressure range 200 to 1000 atm and at a temperature of about 450 °C. Apart from iron, several other metals have been tested as catalysts (e.g., Mo, W, Mn, Ru, etc). By using only the metals as catalysts, there is some degradation in activity. However, by using catalytic promoters, degradation is minimized. The generally accepted mechanism for ammonia synthesis follows the sequence:



Since the adsorption behavior of atomic nitrogen and of hydrogen are of the Temkin type (see Chapter 1), there is a decrease in the activation energy for adsorption with increase of coverage of the intermediate species. The nitrogen-adsorption intermediate step (Eq. 8.29) is the rate-limiting one. The quantity of ammonia production in the USA exceeds 30 million tons/year, and the bulk of it is utilized by the fertilizer industry.

8.4.2.3. Hydrazine. The industrial production of hydrazine uses the Raschig process. It involves the partial oxidation of ammonia using sodium hypochlorite in the presence of gelatin or glue at a temperature in the range of 160

to 180 °C and elevated pressure. The product is a dilute liquor at a concentration of only 2%. It is concentrated by fractional distillation to a product 85 to 100% hydrazine hydrate ($\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$). If anhydrous hydrazine is required, this product is dehydrated using barium oxide or sodium hydroxide. Anhydrous hydrazine can also be obtained from hydrazine sulphate, by its reaction with ammonia.

8.5 Fuel Storage

8.5.1. Hydrogen

8.5.1.1. *Multifold Options but Many Challenges.* Hydrogen is the *ideal* fuel for all types of fuel cells and it is the *pristine* one for PEMFCs and AFCs. Table 8.4 summarizes the investigated methods for hydrogen storage and their performance characteristics. Hydrogen can be stored as a compressed gas, liquid, solid, or combined with chemicals. Each method has some advantages and disadvantages. Technical and economic aspects of these storage methods will be summarized in the following Sections. It is assumed in these Sections that hydrogen is produced on a commercial scale by one or more of the methods described in the preceding Sections. Thus, an energy analysis should deal with the entry of hydrogen into the storage system, any conversion in the storage system and the release of hydrogen for input into the fuel cell. The economic aspects should also be taken into consideration.

Section 8.5.3 considers a techno-economic analysis of hydrogen storage versus alternate fuels, mainly hydrocarbons, alcohols, and ethers. But in these cases, it must be remembered that for the low and intermediate temperature fuel cells, these fuels will have to be converted to hydrogen (see Section 8.2) and for the high temperature fuel cells, to hydrogen plus carbon monoxide. The exceptions are methanol, ethanol, and dimethyl ether that may be used directly in proton-exchange-membrane fuel cells. Another exception, as described in Section 8.2.6, is the case where a fuel, like natural gas, can be fed directly to a MCFC or SOFC and the anode electrocatalyst (or a separate catalyst) converts methane into hydrogen and carbon monoxide, which are then electrooxidized. Energy efficiencies and costs of hydrogen entering the fuel cell will also be taken into consideration in Section 8.5.3.

8.5.1.2. *Compressed Hydrogen Stored Underground for Power Generation.* Large quantities of hydrogen can be stored underground in natural gas fields, aquifers, and salt domes. The capacities can be as large as 1 billion Nm^3 in aquifers or gas fields and several million Nm^3 in caverns. The pressure for storage is about 60 atm. Only a fraction of this amount (one to two thirds) is available for the storage cycle, mainly to maintain a cushion gas pressure. These systems can provide 1 to 10 M Nm^3 of hydrogen. The energy density for hydrogen

TABLE 8.4
Techno-Economic Assessments of Hydrogen Storage Systems

Storage Method	Hydrogen weight (%)	Content (vol g/l)	Energy density (kJ/kg)	Higher heating value (kJ/l)	Relative cost ^a	Demonstrated/ potential applications
Gas						
Steel cylinder (60 kg/50 l/200 atm)	1.5	18	2,132	1,003	2	Lab chemical, transportation
Alumina composite (75 kg/125 l/200 atm)	2.6	17	3,700	1,739	3	Transportation, portable power
Glass microspheres	6	6	8,527	853	5	Scientific curiosity
Zeolites	0.8	6	1,128	814	5	Residential industrial fuel
Liquid						
Cryogenic 300 m ³ semitrailer	12.5	71	17,765	9,919	1	Rocket fuel, space fuel cells
Solid						
FeTiH ₂	1.6	96	2,278	13,564	3	Portable power, transportation
LaNi ₅ H ₆	1.4	89	1,990	12,749	3	
Mg ₂ NiH ₄	3.2	81	4,514	11,474	3	
Combined with Chemicals						
n-Octane	15.8	11	47,652	33,524	1	Transportation
Methanol	12.5	150	22,321	17,665	1	Transportation, portable power
Ammonia	17.6	136	22,363	17,222	1	Farm vehicle, portable power

^aCode for Relative Cost: 1 → Least expensive capital cost (~ \$10/kg of H₂); 5 → Most expensive

is only about one third that for natural gas. Therefore, it is more costly to store hydrogen by this method, not only for this reason, but also due to the production costs of hydrogen from primary energy sources raising the cost of hydrogen. The energy efficiency for this method of storage should take into consideration the electrical energy for compression of the gas. According to some analysis, fuel processing of CH₄ to H₂ is carried out under pressure. Therefore, for further compression of H₂, the energy requirement for energy storage is reduced to about 10% of the fuel energy. Some of this energy may be recovered by using a compressor-expander cycle for the entry of hydrogen into the storage system and its delivery to the fuel cell.

8.5.1.3. Compressed Hydrogen Storage in Cylinders Tanks for Transportation and Portable Power. The most common method for storage of hydrogen on a relatively small scale for automobiles and buses is as a compressed gas in stainless steel cylinders at a pressure of about 130 to 150 bar. The cylinder weight is about 10 kg and its volume is about 40 liters. The hydrogen content is only 0.5 kg. Thus, the specific energy and energy density are very low (see Table 8.4). Considerable efforts have been made to substantially increase the hydrogen content by using light-weight high-strength materials, such as fiber-glass reinforced aluminum and carbon composites, as well as using higher pressures (up to about 350 bar). As seen from Table 8.4, the specific energy and energy density can be improved by about a factor of at least five by using the advanced materials for construction of the cylinders. The electric energy penalty for compression of the hydrogen is about 10% of that in the fuel. Since the lifetime of a cylinder can exceed 5 to 10 years, there is only a marginal cost, which can be added to the cost of the hydrogen.

On a somewhat larger scale and more so for hydrogen distribution stations, one can have above-ground compressed gas storage in pressure tanks. The pressures can be in the range of 100 to 500 bar. These can contain 175,000 to 250,000 liters of hydrogen. Since tank storage of this type is modular, there is only a linear economy for scale-up. Energy penalty and cost for such a method of storage (mainly due to electricity costs for compression and a minor amount due to capital costs) are about 7-10% of the fuel energy and \$3,000-\$5,000/GJ, respectively.

Since the early 1970s, there was some interest in storing hydrogen in glass bead microspheres. The idea was that the glass microspheres could withstand hydrogen pressures up to 700 bar, while the pressure in the container was much less. Thus, from a safety point of view, this method could be considerably better. However, because of the slow rate of breakage of the glass beads with long term repeated cycling with hydrogen (i.e., hydrogen in, hydrogen out), this approach has virtually been abandoned.

8.5.1.4. Liquid Hydrogen Storage for Space, Military, and Transportation Applications. Hydrogen is the lightest fuel in terms of specific energy (kWh/kg) and oxygen is the lightest oxidant. It is for this reason that NASA chose these two chemicals in the cryogenic form for space flights, which last for two weeks or longer. The largest storage vessel used by NASA has a capacity of 3 million liters, corresponding to about 10 million kWh. In the long term space program (e.g., the space station and Mars), it is proposed to use photovoltaic power generators to generate electricity for utilization during the *light* periods, as well as for electrolyzing water (produced from fuel cells) to regenerate hydrogen and oxygen and then liquefy these two gases. The military is also interested in the storage of hydrogen and oxygen cryogenically for fuel cell powered submarines. On the terrestrial front, when large quantities of hydrogen are required and need to be transported, the cryogenic method seems to be the ideal one.

The liquefaction of hydrogen is a highly energy intensive process, theoretically requiring about 3.3 kWh/kg. However, during liquefaction, the ortho-para

conversion of H_2 occurs, and this increases the theoretical energy to about 3.8 kWh/kg. The practical energy requirements are, however, considerably higher, by a factor of about 6 for small liquefiers and 3 for large ones. The net result is that at least 35% of the hydrogen energy is required for the liquefaction process.

The technology for liquefaction of hydrogen typically involves a flow process, as represented in Figure 8.22. Reciprocating compressors had been traditionally used but since centrifugal compressors are more compact and less expensive, there is interest in the use of the latter in more advanced plants. Hydrogen liquefaction involves the use of an admixture of a high molecular weight gas (propane, see

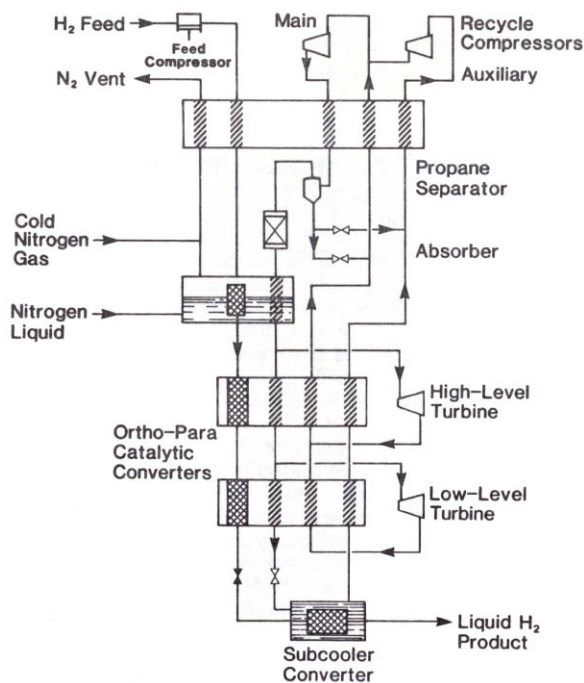


Figure 8.22. Process diagram for liquefaction of hydrogen. Reprinted from Reference 1, Copyright (1985) with permission from John Wiley and Sons.

Figure 8.22) to use the centrifugal compressors more efficiently. The propane gas is subsequently separated from H_2 by liquefaction. The condensate is blended with the hydrogen and fed back to the compressors. Cold nitrogen is introduced at this stage for cooling, and the input of liquid nitrogen provides additional cooling and promotes the ortho to para conversion of hydrogen. The latter is an important step during liquefaction of hydrogen. Since the ortho to para conversion step is

exothermic, efficient heat removal becomes necessary. Use of catalysts can minimize the heat generation and boil-off loss can be minimized. The energy required for the ortho to para conversion (up to 95%) is about 18% of the total energy for the liquefaction process. Four difficulties are associated with the liquefaction process:

- (a) liquefaction of hydrogen occurs at an extremely low temperature, 20.4 K. (cf., BP of methane is 109 K and of N_2 is 78 K). The fall in temperature of gas introduced into a cold tank simulates a cryogenic pump and thus cause introduction of impurities;
- (b) the Joule-Thomson (J-T) inversion temperature for hydrogen (204 K) is below room temperature. An auxiliary liquefaction plant for another gas (e.g., N_2) is thus required to lower the temperature of hydrogen below its J-T inversion temperature. This increases energy costs and energy penalties;
- (c) the refrigeration process is Carnot limited and this efficiency reduces to zero at the absolute zero temperature. The liquefaction temperature is only 20 °C higher; and
- (d) at room temperature the ratio of ortho to para hydrogen is 3:1. The para form has the lower energy. At the temperature of liquefaction, the percentage composition of para is 99.7%. Even though this reaction (ortho to para conversion) is exothermic, it only occurs as the temperature is substantially lowered and thus the energy requirements for liquefaction are high.

Dewar flasks are used to store liquid hydrogen (LH_2). The flask is then immersed in a second one containing liquid nitrogen (LN_2) to prevent heat absorption by thermal radiation.* By having the outer flask containing LN_2 , ΔT is significantly smaller. This method is good only for small quantities of LH_2 (10^5 to 10^6 liters). Using thermal radiation shields positioned within the multilayer insulation, additional heat loss is prevented. The largest LH_2 storage vessels at NASA's Kennedy Space Center are two 3–4 million liter spherical containers. The material for construction of the inner shell (20 m diameter) is austenitic steel. The carbon outer shell has a diameter of 23 m. The operating pressure for the delivery of hydrogen is 6 atm and the boil-off rate is about 0.02%/d, when the tank is full. The capital cost for liquefaction decreases with scale-up, but reaches a steady value at about 225,000 kg/d. LH_2 tanks have also been developed in Germany for delivery of the gas to fuel cells. BMW has demonstrated IC engine powered vehicles with LH_2 . The storage tanks in the vehicles are of the Dewar flask type. The walls are 3 cm thick and contain aluminum foil interlaced with fiberglass matting. More recently, Daimler Benz has also exhibited a fuel-cell automobile, powered with LH_2 . The main difference between the two types of fuel feed to the two vehicles is that in the

* Thermal heat radiation is proportional to ΔT^4 , where ΔT is the temperature difference between LH_2 in the flask and the outside temperature.

former case, hydrogen is delivered in the liquid form, while in the latter, it is in the gaseous form and also heated to the desired temperature. The waste heat from the fuel cells may be efficiently used for this purpose.

In respect to economics, the cost of LH_2 is about \$12/GT for large-scale use. The costs are higher by a factor of 5 to 10 for small-scale use in vehicles. It may be more appropriate to consider LH_2 for use in fleet vehicles, ships, and trains. Apart from the use in the NASA program, LH_2 is used on a large scale by the petroleum refining and ammonia production industries.

8.5.1.5. Solid Storage of Hydrogen as Metal Hydrides. The preceding Sections dealt with the storage of pure hydrogen as a compressed gas and as a liquid. Storing pure hydrogen as a solid is considerably more energy intensive than storing it cryogenically. However, there is one alternate approach in storing hydrogen as a solid, i.e., as a metal hydride. Researchers at Brookhaven National Laboratory in New York, USA and at the Philips Research Laboratory in Eindhoven, Netherlands, both of which started in the 1960s, carried out the pioneering work in this area. Quantum leaps have been made in metal hydride technology, within the last 10 years, mainly for the development and commercialization of nickel/metal hydride batteries. The use of metal hydrides as a source of hydrogen for fuel cells has been the subject of great interest since the 1970s. There has been a multitude of demonstrations of the integration of the metal hydride-storage systems with fuel cells. Other applications of such hydrogen-storage systems include their use in heat pumps and compressors. Metal hydrides consist of three types:

- ionic, e.g., magnesium hydride,
- covalent, e.g., hydrides of Be and of the Group 3 metals, and
- intermetallic, hydrides of the transition and rare earth metals.

For the hydrogen storage application, the ideal type of hydrides is the metals/alloy, which reversibly absorb and desorb hydrogen. An example is given by the Fe-Ti alloy:



The hydrogen absorption/desorption characteristics of a metal or alloy are best represented by the pressure–composition–temperature (P - C - T) isotherms, as illustrated in Figure 8.23. The extent of absorption depends on the equilibrium pressure. The hydrogen molecule dissociatively adsorbs on the metal or alloy. At relatively low pressures, the adsorbed hydrogen diffuses into the bulk and occupies interstitial sites in the metallic lattice and the isotherm ascends steeply as hydrogen absorbs into the metal, forming a solid solution or the α -phase. In Figure 8.23, region A-B signifies a limited amount of hydrogen in the metal or alloy. The region

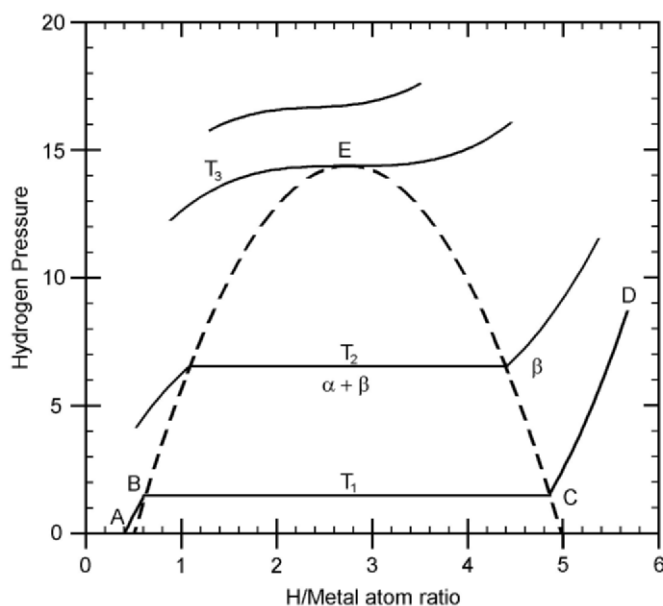


Figure 8.23. Typical pressure-composition-temperature (P-C-T) plots for hydrogen absorption by materials and alloys at three temperatures ($T_1 < T_2 < T_3$).

B-C represents the appearance of a second phase, i.e., the β -phase, which is in equilibrium with the solid solution or α phase. The β -phase is the one in which there is the highest amount of hydrogen absorption into the metal or alloy. According to the Gibbs phase rule, the pressure must be constant in this region, i.e., shown in the Figure as a plateau pressure. After the β -phase region absorbs a saturation amount of hydrogen, it can be further absorbed in the C-D region, but in this region the equilibrium pressure sharply increases with the amount of hydrogen absorbed. With the increase of temperature, the plateau pressure region becomes smaller (see Figure 8.23), accounting for a lower amount of hydrogen absorption. The parabolic curve represents the β -phase region in which hydrogen absorption/desorption occurs as a function of temperature and pressure.

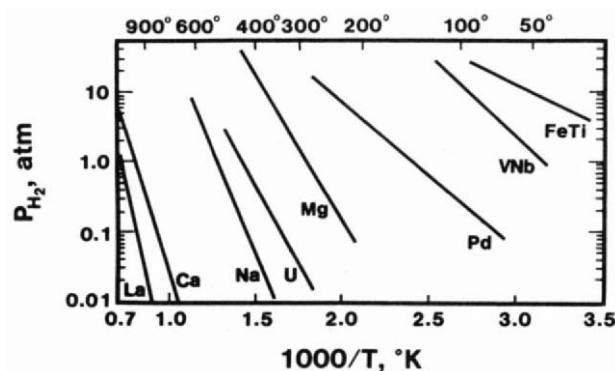


Figure 8.24. Equilibrium pressure for hydrogen absorption of some metals and alloys as a function of temperature. Reprinted from Reference 1, with permission from John Wiley and Sons.

Another plot of importance in selecting the metal hydride systems is that of the equilibrium pressure as a function of temperature (Figure 8.24). The range of pressures that is of interest for a hydrogen storage system for fuel cell applications is about 1 to 5 atm. Also, it is necessary for the hydrogen desorption to occur at below 100 °C. Thus, from Figure 8.24, it can be seen that Fe, Ti, and VNb alloys are potential candidates. Not shown in this graph are the AB₅ and AB₂ alloys, which show considerably better *P-C-T* characteristics. Typical examples of these alloys are LaNi₅ and FeTi₂. The AB₅ alloys are predominantly used for the hydride electrodes in the rechargeable nickel/metal hydride batteries because these have the ideal characteristics of maximum absorption of hydrogen (one atom of hydrogen for each atom of the metal). The alloys are modified with partial substitution of the parent components by other elements (e.g., cerium, copper, tin) which have effects of lowering the plateau pressure, inhibiting the oxidation of the parental elements, and increasing the lattice parameters. The first step in the absorption of hydrogen by the alloy is the dissociative adsorption of hydrogen on the surface of the alloy. This is a catalytic process and nickel, in the alloy LaNi₅, fulfills this role. The oxidation of nickel is inhibited by the presence of small amounts of Ce in the alloy.

As seen from Table 8.4 on a volumetric basis, the hydrogen content in a metal hydride is somewhat higher than for LH₂ and somewhat lower than for hydrogen combined with carbon or nitrogen. However, on a weight % basis, the hydrogen content is lower by a factor of ten, when making such a comparison. Magnesium hydride (MgH₂) has a hydrogen content of 12 %, but its plateau pressure

(dissociation pressure) is too low at room temperature, and it will have to be heated up to a temperature of about 400 °C to increase its dissociation pressure to about 1 atm. Again, alloying magnesium with nickel facilitates the dissociative adsorption of hydrogen, but even in this case, it is necessary to increase the temperature up to about 280 °C to achieve a 1 atm equilibrium pressure of hydrogen. Table 8.4 shows that alloying magnesium with nickel reduces the hydrogen content in the hydride by a factor of about four. To overcome the weight penalty of the FeTiH₂ hydride, Daimler-Benz designed an ingenious dual metal hydride system for storage on board in an IC engine powered vehicle. Only a small quantity of FeTiH₂ was carried for start-up and acceleration. Soon after the exhaust temperature became hot enough, the source of hydrogen was a Mg-Ni hydride, which was the main source of the hydrogen fuel for cruising. Toyota, Honda, and Mazda have demonstrated fuel cell powered vehicles, with hydrogen stored as metal hydrides. In all these cases, the AB₅ alloys were used for the hydrides. Due to the relatively low hydrogen content, the ranges of the vehicles were about 200 km or less with a fully charged storage system.

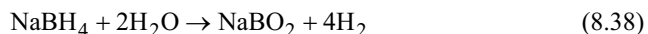
From a safety point of view, the metal hydride storage system is attractive (see Section 8.7) but its disadvantages are the following:

- though the hydrogen content on a volumetric basis is good, on a weight percent basis it is low. Thus, it is not sufficiently competitive with fuel processing to produce hydrogen. In the latter case, one must also take into account the weight and volume of the fuel-processor;
- during hydriding/dehydriding, there is particle attrition. Even though there is some advantage of fine particles for the kinetics of hydriding/dehydriding reactions, from a safety point of view, it is essential that the particles do not reduce to submicron sizes;
- thermal management is critical. Hydriding of a metal is an exothermic reaction and hence, the storage unit needs cooling. Dehydriding, for supply of hydrogen, requires heating. In general, the thermal energies required for these reactions are small with the desired hydrides;
- the kinetics hydriding/dehydriding reactions are very sensitive to impurities (e.g., CO, O₂, and sulphur compounds). The oxygen, present at a critical level, is also a fire hazard. Hydrides in ultra-low particle sizes are pyrophoric; and
- from an economic point of view, hydrogen storage using metals or alloys is quite expensive (of the order of a \$1000/kg of metal hydride).

An alternative approach for application of a metal hydride storage system is to use ionic hydrides such as calcium hydrides (CaH₂), lithium aluminum hydride (LiAlH₄), sodium borohydride (NaBH₄), and a combination of these with water, on site or on board, to generate hydrogen, as for example:

TABLE 8.5
Physical Properties of Hydrogen, Methane, and Gasoline

	Hydrogen	Methane	Gasoline
Molecular weight (g/mole)	2.016	16.04	~ 110 (C _n H _{1.87n})
Mass density (kg/Nm ³) at standard conditions, i.e., <i>P</i> = 1 atm, <i>T</i> = 0 °C	0.09	0.72	720-780 (liquid)
Mass density of liquid H ₂ at -253 °C (kg/Nm ³)	70.9	—	—
Boiling point (K)	20.2	111.6	310-478
Higher heating value (MJ/kg)	142.0	55.5	47.3
Lower heating value (MJ/kg)	120.0	50.0	44.0
Flammability limits (% volume)	4.0-75.0	5.3-15.0	1.0-7.6
Detonability limits (% volume)	18.3-59.0	6.3-13.5	1.1-3.3
Diffusion velocity in air (m/s)	2.0	0.51	0.17
Buoyant velocity in air (m/s)	1.2-9.0	0.8-6.0	non-buoyant
Ignition energy at stoichiometric mixture (mJ)	0.02	0.29	0.24
Ignition energy at lower flammability limit (mJ)	10	20	n.a.
Flame velocity in air (cm/s)	265-325	37-45	37-43



These reactions are quite exothermic and have to be carried out in a highly controlled manner. In the case of NaBH₄, control of the pH and use of a catalyst are essential. Such systems have been proposed for transportation applications. There are several disadvantages for such an approach:

- these hydrides are highly stable and the regeneration of the hydrides from the product of hydrogen generation (e.g., see reverse of Eq. 34, NaBH₄ from NaBO₂) is highly energy intensive and expensive (cost of NaBH₄ is \$45/kg);
- carrying a high quantity of water is essential for the reaction. The weight and volume of the water have to be taken into account in ascertaining the energy density and specific energy of the storage system;

- as stated above, there are safety issues in hydrogen generation from these hydrides when combining them with water. The reactions have to be carried in optimally designed reactors; and
- the hydroxide and oxide products are highly corrosive. This makes the selection of materials for the containers quite challenging.

There is, however, interest in such types of hydrogen storage/hydrogen generation systems for low-power fuel-cell systems (a few W to a few kW).

8.5.2. Hydrogen Storage in Combination with Other Elements or Compounds

The ideal element for hydrogen storage is in combination with carbon as hydrocarbon or alcohols. This topic has been extensively dealt with in Sections 8.1 to 8.3. One interesting carbon-hydrogen system that was not discussed, is the benzene-cyclohexane system. The second most interesting element is nitrogen (see Section 8.4.2). The other possible interesting elements are Be, B, and Si. The hydrides of these elements are quite toxic. In practically all these cases the hydrides are of the covalent type.

8.5.3. Techno-economic Analysis of Hydrogen Storage

Development of a safe, compact, lightweight, and low cost storage for hydrogen is an important issue, particularly for hydrogen vehicles. Also, it is desirable that onboard hydrogen storage vehicles could be rapidly refuelled (< 5 minutes) with a relatively small expenditure of energy, for example, for compression. Recently, the United States Department of Energy set goals for hydrogen storage onboard vehicles (US DOE 2002). Current physical (compressed gas) storage at about 350 bar already satisfies most of these goals, with the exception of volumetric energy density. The simplicity of compressed-gas storage makes it attractive, especially for vehicles like buses, where space constraints are not as stringent as on cars. However, the volumetric energy density is lower for compressed gas than for liquid hydrogen or metal hydrides. For very efficient hydrogen vehicles, the amount of hydrogen energy storage required is acceptably small for a 500-km travel range, and the volume may not be as large a constraint.³¹

The cost and performance of onboard hydrogen-storage systems for fuel-cell vehicles has been estimated by Directed Technologies, Inc. and the Ford Motor Company,^{31,32} assuming that these systems are mass produced. Mass produced costs of \$1000 per car are estimated for advanced compressed gas cylinders holding hydrogen at about 350 bar. Costs for liquid-hydrogen systems are projected to be about \$500 per car. The costs of hydride systems are less well characterized, as these systems are further from commercialization, but are projected to be several thousand dollars per car.

8.6. FUEL TRANSMISSION AND DISTRIBUTION: HYDROGEN VERSUS OTHER ALTERNATE FUELS

Most studies indicate that compressed hydrogen gas is the simplest, near-term option to store hydrogen onboard vehicles. A number of possibilities for producing and delivering compressed gaseous hydrogen transportation fuel to vehicles can be considered, which employ commercial or near commercial technologies for hydrogen production, storage, and distribution. These include:

- hydrogen produced from natural gas in a large, centralized steam-reforming plant and truck delivered as a liquid to refuelling stations;
- hydrogen produced in a large, centralized steam-reforming plant, and delivered via small scale hydrogen gas pipeline to refuelling stations;
- hydrogen from chemical industry sources, e.g., excess capacity in refineries which have recently upgraded their hydrogen production capacity, etc., with pipeline delivery to a refuelling station;
- hydrogen produced at the refuelling station via small scale steam-reforming of natural gas, in either a conventional or an advanced steam-reformer of the type developed as part of fuel cell cogeneration systems; and
- hydrogen produced via small scale water electrolysis at the refuelling station or in residential homes.

In the longer term, other centralized methods of hydrogen production might be used including gasification of biomass, coal or municipal solid waste, or electrolysis powered by wind, solar, or nuclear power. Thermochemical hydrogen production systems might include capture and sequestration of byproduct CO₂.

The capital cost of developing an extensive gaseous-hydrogen refuelling infrastructure for hydrogen fuel-cell vehicles has been estimated by several authors^{31,33-35} to be in the range of several hundred to several thousand dollars per car, depending on the hydrogen supply pathway and level of demand. For the first few demonstration projects, the cost of hydrogen refuelling stations will be considerably higher than this. However, after building several hundreds of large-size hydrogen refuelling stations (serving fleets totaling perhaps several hundred thousand vehicles), refuelling station capital costs should decrease.

The best hydrogen supply option is site-specific, depending on local energy prices, the size of the demand, and the distance from a nearby source of hydrogen. Starting with centrally refuelled fleet vehicle markets would defer the need to build a widespread public hydrogen infrastructure until the technology had been proved and costs had been reduced in fleet use.

The cost of building a hydrogen infrastructure has been compared to the cost of implementing a new infrastructure for other alternative fuels.³³⁻³⁶ Techno-economic analysts have found that the capital cost of hydrogen infrastructure per car, based on various near to mid-term hydrogen supply options, is comparable to that for a methanol infrastructure, assuming high levels of implementation and highly-

efficient hydrogen vehicles.^{34,37} Maintaining the current gasoline infrastructure would be more costly than implementing a new infrastructure based on hydrogen production via onsite reforming of natural gas. A hydrogen infrastructure based on coal with CO₂ sequestration and hydrogen delivery is projected to be more costly than one based on natural gas³⁸ and renewable hydrogen routes are also projected to be more capital intensive.¹⁶

8.7. Fuel Safety: Hydrogen versus Alternate Fuels

When hydrogen is proposed as a future fuel, the average person may ask the question about the Hindenburg, the Challenger, or even the hydrogen bomb disasters. Clearly, consumers will not accept hydrogen or any new fuel unless it is as safe as our current fuels. Table 8.5 shows some safety related physicochemical properties of hydrogen as compared to two commonly accepted fuels natural gas and gasoline.³⁹ In some ways, hydrogen is clearly safer than gasoline. For example, it is very buoyant and disperses quickly from a leak. This contrasts with gasoline, which puddles rather than disperses, and where fumes can build up and persist even outside. Hydrogen is non-toxic, which is also an advantage.

Other aspects of hydrogen are potential safety concerns. Hydrogen is a small molecule and is more likely to leak than other gaseous fuels. Leak prevention, which can be accomplished through proper equipment design and maintenance as well as reliable leak-detection, are key safety issues for hydrogen. Hydrogen can cause embrittlement of certain steels, resulting in cracks, leaks, and failure. However, with properly selected materials, the possibility of embrittlement can be avoided.

Hydrogen has a wide range of flammability and detonability limits, e.g., a wide range of mixtures of hydrogen in air will support a flame or an explosion. In practice, the lower flammability limit is most important. For example, if the hydrogen concentration builds up in a closed space through a leak, problems might be expected when the lower flammability limit is reached. The lower flammability limit is comparable for hydrogen and natural gas.

The ignition energy (e.g., energy required in a spark or thermal source to ignite a flammable mixture of fuel in air) is low for all three fuels compared to real sources such as electrostatic sparks. The ignition energy is about an order of magnitude lower for hydrogen than for methane or gasoline under stoichiometric conditions. But at the lower flammability limit, the point where problems are likely to begin, the ignition energy is about the same for methane and hydrogen. If hydrogen leaks in a closed space, a large volume of flammable mixtures can occur, increasing the likelihood of encountering an ignition source. The flame velocity is high in hydrogen-air mixtures, carrying the risk of a fire transitioning to an explosion in a confined space. For this reason, it is recommended that hydrogen refuelling and storage be done outdoors, whenever feasible, or in well-ventilated indoor areas.

During vehicle refuelling and maintenance, it is important to avoid producing flammable mixtures, by excluding air from storage tanks, refuelling lines, etc. This can be done with double locks on lines, and by maintaining a positive pressure in hydrogen tanks and lines to exclude air. If necessary, lines and tanks should be purged with nitrogen prior to filling with hydrogen. Hydrogen burns with a nearly invisible flame, and radiates little heat, making fire detection difficult in the daytime. However, infrared detectors or special heat sensitive paints on hydrogen equipment allow rapid detection.

Safe handling of large quantities of hydrogen is routine in the chemical industry. Proposed use of hydrogen in vehicles has raised the question of whether this experience can be translated into robust, safe hydrogen vehicles and refuelling systems for the consumer, a topic that has been addressed in several recent papers. Safety engineers at Air Products and Chemicals, Inc., a large producer of chemical hydrogen,^{40,41} delineated procedures for safe operation in hydrogen vehicle refuelling. According to a 1994 hydrogen vehicle safety study by researchers at Sandia National Laboratories⁴²

“...there is abundant evidence that hydrogen can be handled safely, if its unique properties—sometimes better, sometimes worse and sometimes just different from other fuels—are respected.”

A 1997 report on hydrogen safety by Ford Motor Company⁴³ concluded that the safety of a hydrogen fuel cell vehicle would be potentially better than that of a gasoline or propane vehicle, with proper engineering.

To assure that safe practices for using hydrogen fuel are employed and standardized, there has been a considerable effort by industry and government groups within the US and several other countries in recent years to develop codes and standards for hydrogen and fuel-cell systems. Development of low cost, reliable hydrogen sensors is an ongoing area of research.

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PROBLEMS

1. Various analysts have projected that a lightweight, mid-sized hydrogen fuel cell automobile would have an energy consumption of about 12 g of hydrogen/mile in a typical urban-highway driving.
 - (a) How does this compare to the average energy consumption in today's gasoline car? Use the conversion factors below and assume that today's gasoline car has an average fuel economy of 27 miles/gal gasoline.
 - (b) Compare the amount of hydrogen-energy needed by this car in one year to the amount of gasoline-energy needed by today's average US gasoline car. Assume that the vehicle is driven 11,000 miles per year (the US average).
 - (c) There are about 140 million cars in the US. Find the total hydrogen energy use that would be needed for cars in the US, if all the vehicles were efficient hydrogen vehicles. How much energy would be saved in the US by switching to hydrogen vehicles?
 - (d) At present, the US uses about 10 EJ of oil-energy per year for light-duty vehicles, and imports about 15 EJ of oil for all purposes. How much oil could be displaced by switching to fuel-cell vehicles using hydrogen?

Useful Conversion Factors:

- 1 MJ = Megajoule = 10^6 Joules
- 1 GJ = gigajoule = 10^9 Joules
- 1 EJ = exajoule = 10^{18} Joules
- 1 kg H_2 = 120 MJ (lower heating value or LHV basis)
- 1 gallon gasoline = 0.125 GJ (LHV basis)

2. Hydrogen can be produced from fossil fuels such as natural gas or coal.

- (a) Hydrogen can be produced from natural gas at a conversion efficiency of about 80%. The US currently uses about 22 EJ of natural gas per year. How much would natural-gas use be increased if all the cars in the US ran on hydrogen (use results from Problem 8.1)?
 - (b) Hydrogen can be produced from coal at a conversion efficiency of about 65%. The US currently uses 35 EJ of coal per year. How much would coal use be increased if all cars ran on hydrogen?
 - (c) When hydrogen is produced from coal, CO₂ can be captured and sequestered underground. Typically, about 16 kg of CO₂ are captured per kg of H₂ produced. How many tons of CO₂ should be processed per day if H₂ is made from coal with a CO₂ sequestration from 10% of US cars? If one large CO₂ injection well will take 2500-tons CO₂/day, how many wells would be needed to handle the CO₂ from 10% of US cars?
3. Hydrogen can also be produced from a variety of renewable sources. Consider three renewable options for hydrogen production: solar-photovoltaic-powered electrolysis, wind-powered electrolysis, and biomass gasification. Use the following data to find the land requirements in km² to produce enough hydrogen for 100,000 H₂ fuel cell cars:

Biomass energy production: 10 dry tons per hectare per year

1-dry ton of biomass = 20 GJ

Conversion efficiency of biomass to hydrogen = 60%

1 hectare = 10⁴ m²

Solar PV conversion efficiency to electricity = 15%

Electrolysis efficiency = 80%

PV System losses (wiring, PV-electrolyzer coupling) = 10%

Average annual insolation = 200 Watts/m²

Required land area = twice the solar PV array size (to avoid self-shading by adjacent arrays)

Wind power peak production = 1 MW for a wind turbine with a 50 meter rotor diameter.

Spacing for wind power systems = 5 D x 10 D, where D = wind turbine diameter

Wind power capacity factor = 35% (e.g., annual average production = 35% of peak power production)

How much land is needed per car? How does this compare to a typical roof area (100 m²) or lot size for a suburban house (1/4 hectare)?

4. For a gas pipeline of length L , and inlet and outlet pressures of P_1 and P_2 , the volumetric flow rate Q , and the pipeline diameter D , are related as follows:

$$Q = \frac{\pi T_b}{8 P_b} \left(\frac{1}{f} \right)^{0.5} \left(\frac{R}{W_a G T L Z} \right)^{0.5} (P_1^2 - P_2^2)^{0.5} D^{2.5}$$

where:

- Q = flow rate (mN^3/s)
- L = length of pipeline (m)
- R = universal gas constant = $8314.34 \text{ J}/(\text{kg mol K})$
- P_1 = inlet pressure (N/m^2)
- P_2 = outlet pressure (N/m^2)
- W_a = molecular weight of air = 28.97
- G = dimensionless gas specific gravity
= 0.0696 for H_2 , 0.553 for CH_4 , 1.0 for air
- T = gas temperature (K)
- T_b = reference temperature = 298 K
- D = pipe diameter (m)
- P_b = reference pressure = $101325 \text{ N}/\text{m}^2$ (1 atm)
- f = dimensionless friction factor (depends on the flow regime)
- Z = compressibility = 1

For a fully turbulent flow, the *rough pipe* formula can be used:

$$\left(\frac{1}{f}\right)^{0.5} = 4 \log_{10}(3.7D/k) + 2.273$$

where k = roughness factor = 0.0007, and D is given in inches.

The hydrogen output of a large steam-methane reformer is 3 million Nm^3/day . (i) Find the diameter of a 50-km pipeline with an inlet pressure of 7.3 MPa, and an outlet pressure of 1.4 MPa, carrying this amount of hydrogen. (ii) What is the hydrogen-energy flow rate through the pipeline (expressed in MW), given that the heating value of H_2 is about $0.012 \text{ kJ}/\text{Nm}^3$. (iii) How many efficient H_2 fuel-cell cars could this pipeline supply with fuel? (iv) If it is assumed that the pipeline installed capital costs are given by the maximum of \$155,000/km and \$10,000/[km \times (cm of pipeline diameter)], how much does the pipeline cost? What is the capital cost per car to build the pipeline?